

[DOCUMENT NAME]	Application for Patent
[REFERENCE NUMBER]	FSP-03891
[FILING DATE]	28th August 2002
[CONSIGNEE]	The Director General of the Patent Office
[I. P. C.]	B41M 5/26
[INVENTOR]	
[ADDRESS OR RESIDENCE]	c/o FUJI PHOTO FILM CO., LTD. of No. 200 Ohnakazato, Fujinomiya-shi, Shizuoka-ken
[NAME]	Makoto Ono
[APPLICANT]	
[I. D. NUMBER]	000005201
[NAME]	FUJI PHOTO FILM CO., LTD.
[AGENT]	
[I. D. NUMBER]	100079049
[ATTORNEY]	
[NAME]	Jun Nakajima
[TELEPHONE NUMBER]	03-3357-5171
[APPOINTED AGENT]	
[I. D. NUMBER]	100084995
[ATTORNEY]	
[NAME]	Kazuyoshi Kato
[TELEPHONE NUMBER]	03-3357-5171
[APPOINTED AGENT]	
[I. D. NUMBER]	100085279
[ATTORNEY]	
[NAME]	Katsuichi Nishimoto
[TELEPHONE NUMBER]	03-3357-5171
[APPOINTED AGENT]	
[I. D. NUMBER]	100099025
[ATTORNEY]	
[NAME]	Koji Fukuda
[TELEPHONE NUMBER]	03-3357-5171

[INDICATION OF FEE]

[I. D. NUMBER IN ADVANCE PAYMENT REGISTER] 006839

[AMOUNT OF FEE] 21000

[LIST OF FILED DOCUMENT]

[DOCUMENT] Specification 1

[DOCUMENT] Abstract of the Disclosure 1

[GENERAL POWER OF ATTORNEY NUMBER] 9800120

[DOCUMENT NAME] SPECIFICATION

[TITLE OF THE INVENTION]

THERMAL RECORDING MATERIAL

[CLAIMS]

[Claim 1] A thermal recording material comprising, on a support, a thermal recording layer and a protective layer which comprises at least polyvinyl alcohol and two or more kinds of ultrafine inorganic particles having different average particle sizes, wherein the thermal recording material further comprises boric acid and a water-soluble zirconium compound.

[Claim 2] The thermal recording material of claim 1, wherein a content of the boric acid is 10 to 30 % by mass based on the entire polyvinyl alcohol contained in the thermal recording material, and a content of the water-soluble zirconium compound is 0.1 to 10 % by mass based on a content of the entire polyvinyl alcohol contained in the thermal recording material.

[Claim 3] The thermal recording material of claim 1, wherein at least one kind of the ultrafine inorganic particles is colloidal silica having an average particle size of 10 to 50 nm.

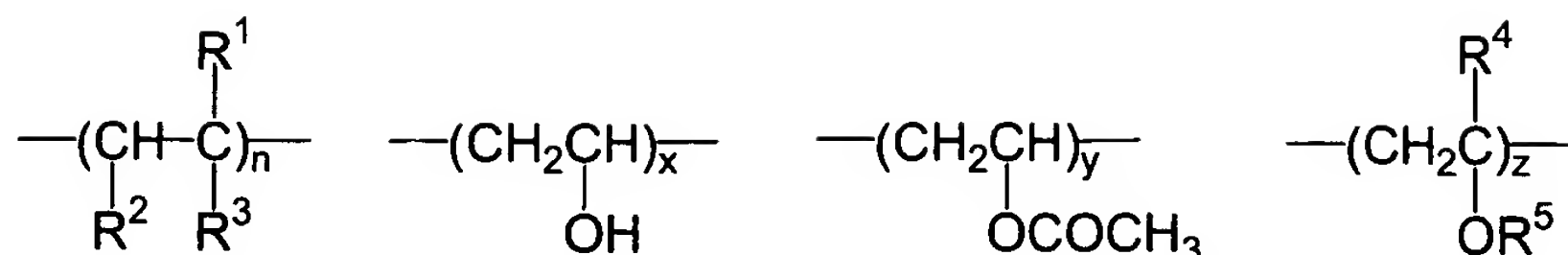
[Claim 4] The thermal recording material of claim 3, wherein the other kind of the ultrafine inorganic particles is barium sulfate having an average particle size of 0.05 to 0.20 nm, and a composition ratio of the colloidal silica to the barium sulfate is 8 to 24 % by mass.

[Claim 5] The thermal recording material of claim 1, wherein the polyvinyl alcohol is a long-chain alkyl ether-modified polyvinyl alcohol.

[Claim 6] The thermal recording material of claim 5, wherein the long-chain alkyl ether-modified polyvinyl alcohol is a polyvinyl alcohol, which is modified with an alkyl ether group having 8 to 20 carbon atoms.

[Claim 7] The thermal recording material of claim 5, wherein the long-chain alkyl ether-modified polyvinyl alcohol is a polyvinyl alcohol which is represented by the following general formula (A):

General formula (A)



wherein in general formula (A), R¹ represents a hydrogen atom, a methyl group or -CH₂CO₂M; R² represents a hydrogen atom, or -CO₂M; R³ represents a hydrogen atom, -CO₂M, an amino group, an amido group, a substituted amido group, a hydroxyl group, a glycidyl group, a sulfonic acid group, a polyethylene oxide group, a polypropylene oxide group or a group having these functional groups ; R⁴ represents a hydrogen atom or a methyl group; R⁵ represents an alkyl group having 8 to 20 carbon atoms; M represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, Na, K or Li; and n, x, y and z each represent a degree of polymerization.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

The present invention relates to a thermal recording material for recording an image with a thermal head, more particularly, to a multi-color thermal recording material adapted for recording images multiple times on the same surface under high-speed and high-energy conditions.

[0002]

[Prior Art]

The need for thermal recording systems is expanding in various fields such as facsimiles, printers, and labeling devices, and accompanying that need is a demand for thermal recording materials of higher performance and high-quality images.

In thermal recording materials for image recording by imagewise heating with a thermal head, it is important that the materials not only have properties matching the thermal head, the material and the shape of the protective film of the thermal head, but that they also stably produce high-quality images over a prolonged period of time without generating dirt or abrasions in the thermal head.

[0003]

The protective layer, which resides on the uppermost layer, determines such a thermal head property of a thermal recording material. Various investigations and improvements have been made for protective layers. For example, the addition of a pigment is considered effective for preventing a protective layer from sticking to the thermal head, and improving the image recording property.

It is also considered necessary to increase the proportion of the pigment or to increase the particle size of the pigment, in order to reduce dirt or smudging in the thermal head. However, an increase in the proportion or particle size of the pigment results in a loss of glossiness due to decreased surface smoothness of the protective layer, thereby leading to quality deterioration. Further, when a diazo compound is employed as a color forming agent, the permeability of gases such as oxygen increases, which in turn causes an increase in background coloration when the material is exposed to light.

[0004]

In contrast to an ordinary monochromatic thermal recording material, a full-color thermal recording material is subjected to three consecutive printing operations on the same surface, under high-speed and high-energy conditions. Therefore, the surface temperature of the thermal head reaches a high temperature and the lubricant on the surface of the thermal recording material decreases when printing, and dirt or smudging tends to be generated in the thermal head. Moreover, when considering quality, it is difficult to adopt the aforementioned known technologies (such as increasing the proportion of the

pigment or increasing the particle size of the pigment), in order to achieve high surface gloss and low background coloration by exposure to light.

[0005]

[Problems to be Solved by the Invention]

Accordingly, the invention was made in view of above problems. The object is to provide a thermal recording material having high glossiness and the capability to prevent dirtying of the thermal head, thereby improving the durability of the thermal head and stably providing high-quality images and the problem is to attain the object.

[0006]

[Means for Solving the Problems]

The aforementioned problems can be solved by the following means. The present invention provides:

<1> A thermal recording material comprising, on a support, a thermal recording layer and a protective layer which comprises at least polyvinyl alcohol and two or more kinds of ultrafine inorganic particles having different average particle sizes, wherein the thermal recording material further comprises boric acid and a water-soluble zirconium compound.

<2> The thermal recording material of <1>, wherein a content of the boric acid is 10 to 30 % by mass based on the entire polyvinyl alcohol contained in the thermal recording material, and a content of the water-soluble zirconium compound is 0.1 to 10 % by mass based on a content of the entire polyvinyl alcohol contained in the thermal recording material.

<3> The thermal recording material of <1>, wherein at least one kind of the ultrafine inorganic particles is colloidal silica having an average particle size of 10 to 50 nm.

<4> The thermal recording material of <3>, wherein the other kind of the ultrafine inorganic particles is barium sulfate having an average particle size of 0.05 to 0.20 nm, and a composition ratio of the colloidal silica to the barium sulfate is 8 to 24 % by mass.

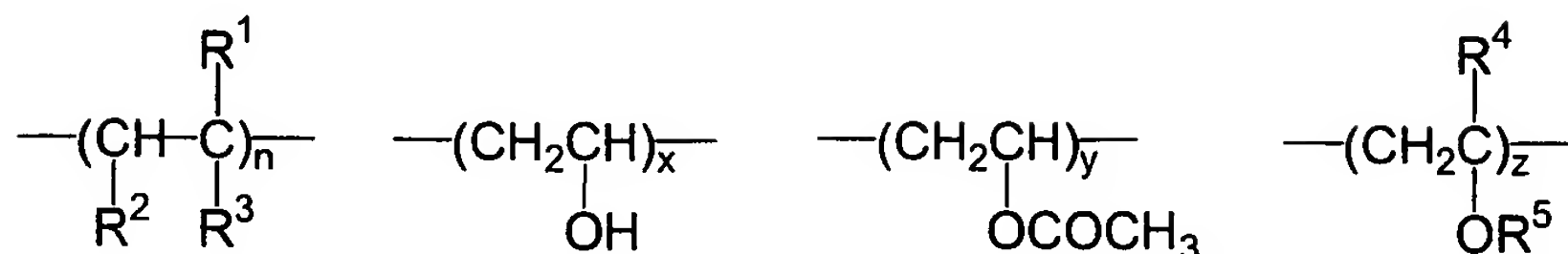
<5> The thermal recording material of <1>, wherein the polyvinyl alcohol is a long-chain alkyl ether-modified polyvinyl alcohol.

<6> The thermal recording material of <5>, wherein the long-chain alkyl ether-modified polyvinyl alcohol is a polyvinyl alcohol, which is modified with an alkyl ether group having 8 to 20 carbon atoms.

<7> The thermal recording material of <5>, wherein the long-chain alkyl ether-modified polyvinyl alcohol is a

polyvinyl alcohol which is represented by the following general formula (A):

General formula (A)



wherein in general formula (A), R¹ represents a hydrogen atom, a methyl group or -CH₂CO₂M; R² represents a hydrogen atom, or -CO₂M; R³ represents a hydrogen atom, -CO₂M, an amino group, an amido group, a substituted amido group, a hydroxyl group, a glycidyl group, a sulfonic acid group, a polyethylene oxide group, a polypropylene oxide group or a group having these functional groups ; R⁴ represents a hydrogen atom or a methyl group; R⁵ represents an alkyl group having 8 to 20 carbon atoms; M represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, Na, K or Li; and n, x, y and z each represent a degree of polymerization.

[0007]

[Embodiments]

The thermal recording material of the present invention is characterized in that it includes, on a support, a thermal recording layer and a protective layer

containing at least polyvinyl alcohol and two or more kinds of ultrafine inorganic particles with different average particle sizes, and further includes boric acid and a water-soluble zirconium compound.

[0008]

Owing to the configuration using polyvinyl alcohol as the binder resin of the protective layer and including two or more kinds of ultrafine inorganic particles with different average particle sizes as fillers, the thermal recording material of the invention is capable of exhibiting high hardness while maintaining surface smoothness. Further, boric acid and a water-soluble zirconium compound used in combination provide high hardness while stably realizing the desired lubricating property on the surface of the thermal recording material.

The thermal recording material of the present invention exhibits high glossiness by maintaining high surface smoothness, also, the high surface hardness and stable lubricating property on the surface helps prevent dirtying of the thermal head. This serves to improve the durability of the head and to stably provide high-quality images.

[0009]

In the thermal recording material of this invention, a thermal recording layer and a protective layer are provided in this order on a support, but another layer may also be provided suitably selected according to the purpose, such as an undercoat layer provided between the support and the thermal recording layer, an intermediate layer provided between the plurality of thermal recording layers, or a light transmittance control layer provided between the thermal recording layer and the protective layer.

Further, in the invention, the boric acid and the water-soluble zirconium compound may be included in a coating solution for the protective layer or in a coating solution for the thermal recording layer. Alternatively, they may be included in a coating solution for forming other layers. In case no particular inconvenience is encountered, they may be included in the coating solution for the protective layer or for the thermal recording layer. However, in case an undesirable reaction or interaction with another component is anticipated, it is possible to adopt a method of including them, for example, in the coating solution for the intermediate layer and transferring them to the desired layer by diffusion.

Hereinafter, principal layers which constitute this invention and constituents thereof will be explained in

detail.

[0010]

<Protective layer>

The protective layer is provided in order to improve sticking characteristics of the thermal recording layer and to protect the thermal recording layer from solvent or external air. The protective layer in the invention at least includes polyvinyl alcohol resin as a binder, and two or more kinds of ultrafine inorganic particles, acting as fillers, having different average particle sizes, and may contain other various additives or fillers if necessary.

[0011]

(Polyvinyl alcohol)

Polyvinyl alcohol is employed as a binder resin for the protective layer of the invention. The polyvinyl alcohol can be suitably selected among known polyvinyl alcohols as long as they do not hinder the effect of the invention, and specific examples include those described in JP-A No. 2000-118133.

The polyvinyl alcohol in the invention preferably has an average polymerization degree of 600 to 2000, and more preferably 1200 to 1800.

Polyvinyl alcohol to be employed in the invention includes a derivative thereof. This derivative polyvinyl alcohol is preferably alkyl ether-modified polyvinyl alcohol, silanol-modified polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, a hydrophobic group-modified polyvinyl alcohol, ethylene-modified polyvinyl alcohol, or itaconic acid-modified polyvinyl alcohol, and alkyl ether-modified polyvinyl alcohol is particularly preferred.

[0012]

In the protective layer of the invention, another binder may be used in combination with polyvinyl alcohol, if necessary. Examples of such binders include a water-soluble polymer such as vinyl acetate-acrylamide copolymer, silicon-modified polyvinyl alcohol, starch, denatured starch, methyl cellulose, carboxymethyl cellulose, hydroxymethyl cellulose, gelatin, gum Arabic, casein, a hydrolysate of a styrene-maleic acid copolymer, a hydrolysate of a styrene-maleic acid copolymer half ester, a hydrolysate of an isobutylene-maleic anhydride copolymer, a polyacrylamide derivative, polyvinylpyrrolidone, sodium polystyrenesulfonate, and sodium alginate, and a synthetic rubber latex or a synthetic resin emulsion such as a styrene-butadiene rubber latex, an acrylonitrile-butadiene rubber latex, a

methyl acrylate-butadiene rubber latex, or a vinyl acetate emulsion.

[0013]

The polyvinyl alcohol constituting the aforementioned binder has a Tg (glass transition point) of 150°C or lower, preferably of 0°C to 130°C and particularly preferably of 40°C to 100°C.

[0014]

The content amount of the binder in the protective layer is preferably 25 to 80 % by mass and more preferably 40 to 70 % by mass. In case another binder is employed in combination, it is preferred that all the binders meet the aforementioned content.

[0015]

(Long-chain alkyl ether-modified polyvinyl alcohol)

The thermal recording material of the present invention preferably employs a long-chain alkyl ether-modified polyvinyl alcohol, as the alkyl ether-modified polyvinyl alcohol. The use of such long-chain alkyl ether-modified polyvinyl alcohol improves dispersibility of the ultrafine inorganic particles employed as the filler, thereby improving the surface smoothness of the

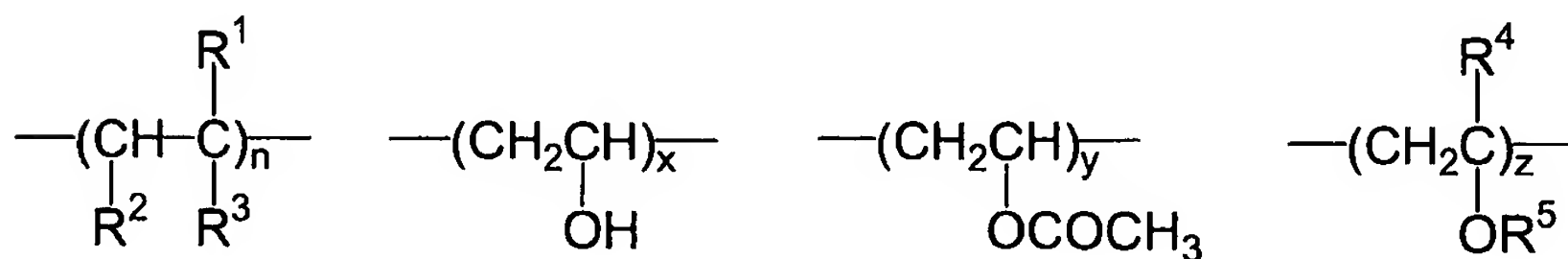
thermal recording material and compensating for loss in glossiness resulting from addition of the ultrafine inorganic particles.

[0016]

The long-chain alkyl ether-modified polyvinyl alcohol preferably includes an alkyl group with 8 to 20 carbon atoms. The long-chain alkyl ether-modified polyvinyl alcohol is more preferably a polymer represented by the following general formula (A):

[0017]

General formula (A)



[0018]

In general formula (A), R^1 represents a hydrogen atom, a methyl group or $-\text{CH}_2\text{CO}_2\text{M}$; R^2 represents a hydrogen atom, or $-\text{CO}_2\text{M}$; R^3 represents a hydrogen atom, $-\text{CO}_2\text{M}$, an amino group, an amido group, a substituted amido group, a hydroxyl group, a glycidyl group, a sulfonic acid group, a polyethylene oxide group, a polypropylene oxide group or a

group having these functional groups; and R^4 represents a hydrogen atom or a methyl group.

The combination is preferred in which R^1 , R^2 and R^4 are hydrogen atoms and R^3 is $-\text{CO}_2\text{M}$, or a combination in which R^2 and R^4 are hydrogen atoms, R^1 is $-\text{CH}_2\text{CO}_2\text{M}$ and R^3 is $-\text{CO}_2\text{M}$.

[0019]

In the foregoing general formula (A), M represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, Na, K or Li.

[0020]

In the foregoing general formula (A), R^5 represents a long-chain alkyl group i.e., an alkyl group (with 8 or more carbon atoms, preferably 8 to 20 carbon atoms). The alkyl group may be a normal chain or a branched chain. Also, the alkyl group may have a substituent such as an aryl group. The alkyl group is more preferably with 8 to 16 carbon atoms for improving a lubricating property, and particularly preferably, a dodecyl group with 12 carbon atoms.

[0021]

In the foregoing general formula (A), n, x, y and z

each represent a degree of polymerization. n is preferably 0 to 20, more preferably 0 to 10. A large value of n increases acidic groups, thereby improving mutual solubility with gelatin. In order to exploit the characteristics of polyvinyl alcohol, such as a gas barrier property at or under Tg (glass transition point), x is preferably 60 to 99, more preferably 75 to 95. Also, y is preferably 0 to 20. A value of z is preferably larger in consideration of friction resistance with the thermal recording head and lubricating property. However, since z is limited by the solubility and viscosity of an aqueous solution, it is preferably within a range of 0.5 to 10 % based on the total sum of n, x, y and z, more preferably 1 to 5 %.

[0022]

The aforementioned long-chain alkyl ether-modified polyvinyl alcohol preferably has a Tg of 50°C or higher, more preferably 60°C or higher. Scratch resistance is also not deteriorated when the glass transition point (Tg) is equal to or higher than 50°C.

[0023]

The long-chain alkyl ether-modified polyvinyl alcohol is preferably contained in an amount of 50 % by

mass or higher in the total binder of the protective layer, and more preferably at 80 % by mass or higher. Adjusting the content of the long-chain alkyl ether-modified polyvinyl alcohol so as to be equal to or higher than 50 % by mass allows the long-chain alkyl ether-modified polyvinyl alcohol to fully exhibit the aforementioned characteristics.

[0024]

Long-chain alkyl groups tend to orient easily on the surface of a protective layer employing the long-chain alkyl ether-modified polyvinyl alcohol. Such an oriented surface reduces printing torque, thereby avoiding printing failure, and it is therefore possible to improve smoothness (glossiness) of the print surface and color developing density. Also, decreased static friction and dynamic friction on the surface of the protective layer provide good running ability of a medium on a printer. Furthermore, the long-chain alkyl ether-modified polyvinyl alcohol not only exhibits characteristics of excellent light fastness and film strength, which characterize the polyvinyl alcohol system, but also has hydrophobic groups oriented on the surface, which improves the water-resistance of the protective layer.

[0025]

In the protective layer of the invention, in addition to the long-chain alkyl ether-modified polyvinyl alcohol, another binder may also be employed if necessary. Examples of such binders include a water-soluble polymer such as vinyl acetate-acrylamide copolymer, silicon-modified polyvinyl alcohol, starch, denatured starch, methyl cellulose, carboxymethyl cellulose, hydroxymethyl cellulose, gelatin, gum Arabic, casein, a hydrolysate of a styrene-maleic acid copolymer, a hydrolysate of a styrene-maleic acid copolymer half ester, a hydrolysate of an isobutylene-maleic anhydride copolymer, a polyacrylamide derivative, polyvinylpyrrolidone, sodium polystyrenesulfonate, and sodium alginate, and a synthetic rubber latex or a synthetic resin emulsion such as a styrene-butadiene rubber latex, an acrylonitrile-butadiene rubber latex, a methyl acrylate-butadiene rubber latex or a vinyl acetate emulsion.

[0026]

Among these binders, polyvinyl alcohol or a derivative thereof are preferred (hereinafter, collectively referred to as "polyvinyl alcohol"), and specific examples include those described in JP-A No. 2000-118133.

[0027]

A polymer constituting the aforementioned binder has a Tg of 150°C or lower, preferably of 0°C to 130°C and particularly preferably of 40°C to 100°C.

[0028]

The content amount of the binder in the protective layer is preferably 25 to 80 % by mass based on the entire protective layer, and more preferably 40 to 70 % by mass.

[0029]

(Boric acid)

In the thermal recording material of the present invention, boric acid, which is a hardening agent for the aforementioned polyvinyl alcohol, is included in order to increase the hardness and strength of the protective layer. The content of boric acid in the thermal recording material is preferably 10 to 30 % by mass based on the total amount of polyvinyl alcohol employed in layers provided at a recording surface side of the thermal recording material, more preferably 14 to 28 % by mass and most preferably 18 to 24 % by mass. Boric acid contained within these ranges based on the total amount of polyvinyl alcohol employed in the thermal recording material can

sufficiently harden the protective layer and the like, and can inhibit diffusion of the lubricant when printing thereby preventing a decrease in the hydrophobicity of the surface of the protective layer. Conventionally, loss of hydrophobicity is that cause of deterioration in image quality or glossiness.

[0030]

In the process of forming various layers on the support, the boric acid to be employed in the invention may be added in a coating solution for any layer. It can be added to a coating solution for any layer employing polyvinyl alcohol resin, including the protective layer, by regulating the pH value of such a coating solution. Among these, boric acid functioning as a hardening agent in the invention is preferably added to a coating solution for the intermediate layer in order to prevent an undesirable reaction or an undesirable interaction with another component. Boric acid added in the coating solution for the intermediate layer or the like can promptly diffuse to other layers, almost simultaneously with the coating of each coating solution on the support for forming the protective layer, the thermal recording layer and the intermediate layer on the support, thereby causing a crosslinking reaction with polyvinyl alcohol

contained in the coating solution for the protective layer, etc.

[0031]

Here, as the hardening agent, a known crosslinking agent other than boric acid may be employed in combination as long as it does not inhibit the effect of the invention. Examples of such known crosslinking agents include a vinyl sulfone compound, an aldehyde compound (e.g., formaldehyde, glutaraldehyde, etc.), an epoxy compound, an oxazine compound, a triazine compound, the polymer hardening agent described in JP-A No. 62-234157, a methylated melamine, a blocked isocyanate, a methylol compound and a carbodimide resin.

[0032]

(Water-soluble zirconium compound)

In the thermal recording material of the invention, a water-soluble zirconium compound is included in addition to the boric acid mentioned above for the purpose of reducing image unevenness due to load change and decreasing printing torque, thereby reducing unevenness in the density.

The content of the water-soluble zirconium compound in the thermal recording material is preferably 0.1 to 10

% by mass based on the total amount of polyvinyl alcohol employed in layers at a recording surface side of the thermal recording material, more preferably 0.3 to 8 % by mass and most preferably 0.5 to 6 % by mass. A content of the water soluble zirconium compound with less than 0.1% by mass based on the entire vinyl alcohol of the thermal recording material can sufficiently reduce printing torque in the protective layer. Also, the content of the water-soluble zirconium compound exceeding 10% by mass can prevent inducing loss in the glossiness by interaction with a dispersion of fine inorganic particles or an emulsion of lubricant fine particles present together.

[0033]

The water-soluble zirconium compound to be employed in the thermal recording material of the invention can be a metal salt or a complex of zirconium. In the present specification, a "water-soluble zirconium compound" means a compound having a solubility of 1 g or higher in 100 g of water of 25°C, the solubility being preferably 5 g or higher and more preferably 10 g or higher.

Specific examples of the water-soluble zirconium compound include zirconium acetylacetonate, zirconyl acetate, zirconyl sulfate, zirconium ammonium carbonate, zirconium potassium carbonate, zirconyl octylate, zirconyl

nitrate, zirconium oxychloride, and zirconium hydroxychloride.

Among these, zirconyl acetate, zirconium ammonium carbonate, zirconium potassium carbonate or zirconyl nitrate are particularly preferred.

Also, commercially available water-soluble zirconium compounds can be advantageously employed, such as those manufactured by Newtex Co. under the trade names Zircosol AC7, Zircosol HA, Zircosol ZA-2 and Zircosol ZN.

[0034]

In a process of forming various layers on the support, the water-soluble zirconium compound to be employed in the invention may be added in a coating solution for any layer. Among these, the water-soluble zirconium compound may be directly added to a coating solution for the protective layer, in case no undesirable reaction or interaction with another component is anticipated. Otherwise, it may be added in a coating solution for the intermediate layer. In this case, the water-soluble zirconium compound added to the coating solution diffuses to other layers, almost simultaneously with the coating of each coating solution on the support for forming different layers. Thus the water-soluble zirconium compound promptly moves to the protective layer

and exhibits its effect.

[0035]

The water-soluble zirconium compound may be used in combination with a known water-soluble metal salt or a known hydrophobic metal salt compound, as long as it does not inhibit the effect of the invention. Examples of such usable compounds include metal salt or a complex of magnesium, aluminum, calcium, scandium, titanium vanadium, manganese, iron, nickel, copper, zinc, gallium, germanium, strontium, yttrium, molybdenum, indium, barium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, ytterbium, hafnium, tungsten and bismuth.

[0036]

(Ultrafine inorganic particles)

In order to realize high hardness while maintaining surface smoothness, the protective layer of the invention includes two or more types of ultrafine inorganic particles having different average particle sizes, in addition to polyvinyl alcohol.

[0037]

In the specification, the term "ultrafine inorganic

particles" refers to ultrafine inorganic particles with an average primary particle size of 0.5 μm or less, preferably 0.2 μm or less and more preferably of 0.15 μm or less. Any fine inorganic particles meeting these conditions may be used, without any particular restriction. However, these fine inorganic particles preferably have a maximum particle size in a dispersion (i.e., a threshold level at a larger side of the particle size distribution in a dispersion) of 0.5 μm or less, more preferably 0.4 μm or less and particularly preferably 0.35 μm or less. It is also preferred that the frequency of (coagulated) particles having an average particle size of 0.35 μm or greater in a dispersion is 5% or less, preferably 1% or less, and it is particularly preferable that the frequency of (coagulated) particles having an average particle size of 0.25 μm or greater in a dispersion is 5% or less. Such particle size can be measured by known methods, for example, using a submicron particle size analyzer Coulter N4 manufactured by Nikkaki Co.

[0038]

The ultrafine inorganic particles employed in the present invention can be, for example, colloidal silica, barium sulfate, zinc oxide, magnesium oxide, lead oxide,

zirconium oxide, or alumina, among which preferred are colloidal silica, barium sulfate and alumina. Particularly preferred are colloidal silica with an average particle size of 10 to 50 nm and barium sulfate with an average particle size of 0.05 to 0.20 μm , as these are less susceptible to the influence of a charge or a pH value and show high dispersion stability in a coating solution for the protective layer.

[0039]

Specific examples of the ultrafine inorganic particles advantageously employable in the invention include barium sulfate (trade name: BARIFINE BF-21, BF-20, manufactured by Sakai Chemical Industries, Co.); colloidal silica (trade name: Snowtex O, manufactured by Nissan Chemical Ltd.); zirconium oxide (trade name: NZR-A, manufactured by Nissan Chemical Ltd.); zinc oxide (trade name: FINEX-75, manufactured by Sakai Chemical Industries, Co.); titanium oxide (trade name: TTO-55, manufactured by Ishihara Sangyo Co.); and silica (trade name: AEROSIL 200, manufactured by Nippon Aerosil Co.).

[0040]

The protective layer of the present invention includes two or more kinds of the ultrafine inorganic

particles of different average particle sizes. As at least one type of ultrafine inorganic particle, colloidal silica with an average particle size of 10 to 50 nm are preferably included. It is preferred to employ a combination of such colloidal silica and, as at least two types, barium sulfate with an average particle size of 0.05 to 0.20 μm , and it is also preferred that the amount of colloidal silica is 8 to 24 % by mass based on the barium sulfate.

Use of colloidal silica of such ultra-small particle size makes it possible to achieve high hardness while maintaining the smoothness of the surface. In case colloidal silica are used alone, the lubricant may diffuse and may not be retained on the surface of the thermal recording material, due to the high hydrophilicity thereof. However, combined use of barium sulfate makes stable retention of the necessary lubricating property on the surface of the thermal recording material possible. Thus, the thermal recording material of the present invention maintains surface smoothness thereby achieving high glossiness, and also maintains high hardness on the surface. Further, the thermal recording material of the invention, by stably retaining the lubricating property on the surface, is capable of preventing dirtying of the thermal head and improving the durability of the head.

This makes it possible to stably obtain high-quality images.

[0041]

The average particle size of the barium sulfate is preferably 0.05 to 0.20 μm , and more preferably 0.10 to 0.15 μm . The average particle size of the colloidal silica is preferably 10 to 50 nm, more preferably 10 to 30 nm, and most preferably 15 to 25 nm.

Moreover, the amount of the colloidal silica in the protective layer is preferably 8 to 24 % by mass based on the barium sulfate, more preferably 8 to 16 % by mass, and particularly preferably 8 to 10 % by mass. If the average particle sizes of the barium sulfate and colloidal silica are not within the above-mentioned ranges and the content proportion of colloidal silica to barium sulfate is not within the above-mentioned range, the thermal recording material may not maintain high glossiness and avoid conspicuous dirt of the head, thereby enabling trouble-free formation of a multitude of images.

[0042]

In the invention, the preferred amount of barium sulfate and colloidal silica is 60 % by mass or higher in the total ultrafine inorganic particles, more preferably

75 % by mass or higher and particularly preferably 85 % by mass or higher. The presence of barium sulfate and colloidal silica in an amount of 60 % by mass or higher ensures full exhibition of the aforementioned effects.

[0043]

In the present invention, for the method of adding the ultrafine inorganic particles, it is preferable to add a resin solution containing an aqueous dispersible resin such as carboxymethyl cellulose, gelatin or polyvinyl alcohol, or to use a method of addition where the colloidal dispersion of ultrafine inorganic particles prepared in various mills is added. This is in order to avoid mutual coagulation of the particles, and achieve uniform adsorption on the surface of the resin particles, thereby obtaining the desired effects and facilitating manufacture.

Also, the proportion of the binder resin and the ultrafine inorganic particles (binder/ultrafine inorganic particles) in a mass ratio is preferably 0.8/0.5 to 0.8/0.15, and more preferably 0.8/0.45 to 0.8/0.3.

[0044]

An inorganic layered compound such as mica, or a pigment such as calcium oxide, zinc oxide, titanium oxide,

aluminum hydroxide, caolin, a synthetic silicate salt, amorphous silica or an urea-formalin resin powder may be added to the protective layer.

[0045]

(Thermal recording layer)

In the thermal recording material of the present invention, there are preferably provided, as photo-fixable thermal recording layers, a photo-fixable thermal recording layer including a diazonium salt compound having a maximum absorption wavelength at 365 ± 40 nm and a coupler compound capable of forming a color by reaction with the diazonium salt compound, and a photo-fixable thermal recording layer including a diazonium compound having a maximum absorption wavelength of 425 ± 40 nm and a coupler compound capable of forming a color by reaction with the diazonium salt compound.

[0046]

The thermal recording material of the present invention is applicable also to a configuration including a photo-fixable thermal recording layer including a diazonium salt compound having a maximum absorption wavelength of less than 380 nm and a coupler capable of forming a color by reaction with the diazonium salt

compound, and a photo-fixable thermal recording layer including a diazonium salt compound having a maximum absorption wavelength exceeding 390 nm and a coupler compound capable of forming a color by reaction with the diazonium salt compound.

[0047]

Also, in the case of multiple photo-fixable thermal recording layers, a multi-color thermal recording material can be obtained by changing the color hues of the photo-fixable thermal recording layers. More specifically, full-color image recording is possible by selecting three primary colors in the subtractive color mixing, namely yellow, magenta and cyan, for the color hues to be formed in these photo-fixable thermal recording layers. In this case, the color forming mechanism of a photo-fixable thermal recording layer to be directly laminated on the support (i.e., the lowermost photo-fixable thermal recording layer) is not limited to a combination of an electron donating dye and an electron accepting dye, but can also be a diazo color forming system based on a diazonium salt and a coupler capable of reacting with the diazonium salt to form a color, a base color forming system for forming a color by contact with a basic compound, a chelate color forming system or a color

forming system capable of causing a cleavage reaction in contact with a nucleophilic agent to form a color. In such a photo-fixable thermal recording layer, there are preferably provided two or more photo-fixable thermal recording layers, each containing a diazonium salt compound having a respectively different maximum absorption wavelength and a coupler compound capable of forming a color by reaction with the diazonium salt compound.

[0048]

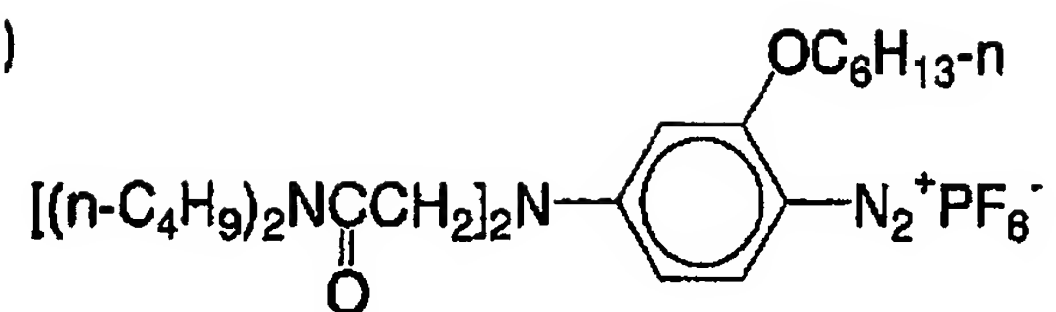
In the invention, any well-known component may be used as a color forming component to be employed in the photo-fixable thermal recording layer. In particular, it is preferred to use a color forming component utilizing a reaction of a diazonium salt compound and a coupler compound, or utilizing a reaction of an electron donating colorless dye and an electron accepting compound. Examples of compounds to be employed in a photo-fixable thermal recording layer including the diazonium salt compound and the coupler include, in addition to such diazonium salt compound and such coupler compound, a base substance capable of accelerating the reaction of the diazonium salt compound and the coupler. These diazonium salt compounds, coupler compounds and base substances are

described in detail, for example, in JP-B Nos. 4-75147, 6-55546 and 6-79867, JP-A Nos. 4-201483, 60-49991, 60-242094, 61-5983, 63-87125, 4-59287, 5-185717, 7-88356, 7-96671, 8-324129, 9-38389, 5-185736, 5-8544, 59-190866, 62-55190, 60-6493, 60-259492, 63-318546, 4-65291, 5-185736, 5-204089, 8-310133, 8-324129, 9-156229 and 9-175017. Specific examples of these materials are shown below, but the invention is not limited to such examples.

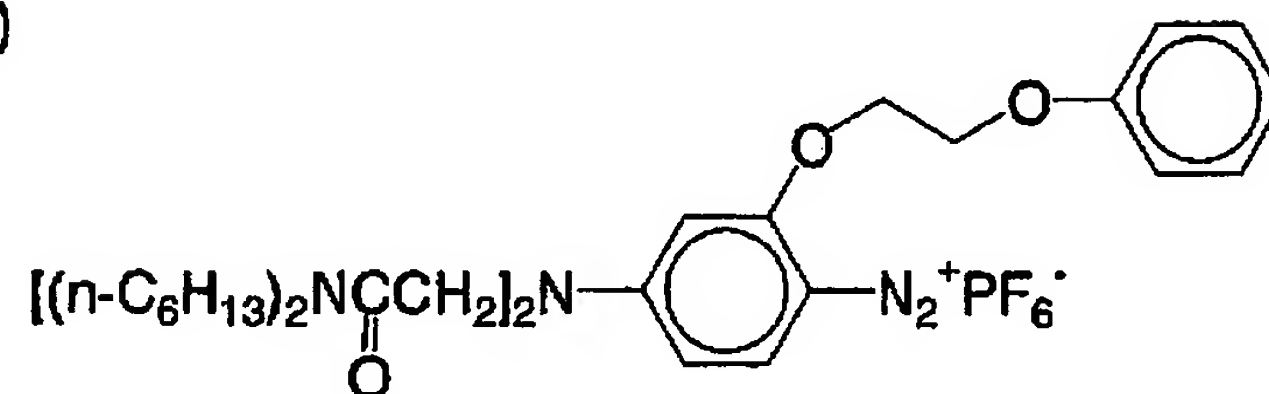
[0049]

-Specific examples of diazonium salt compound-

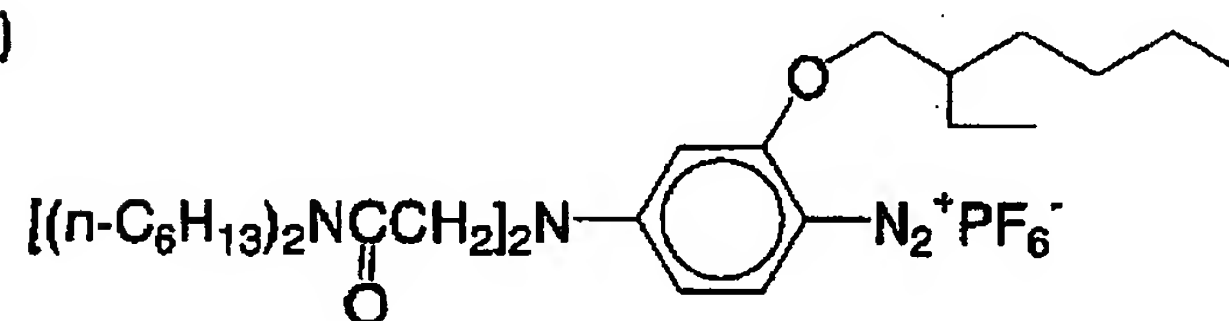
(A-1)



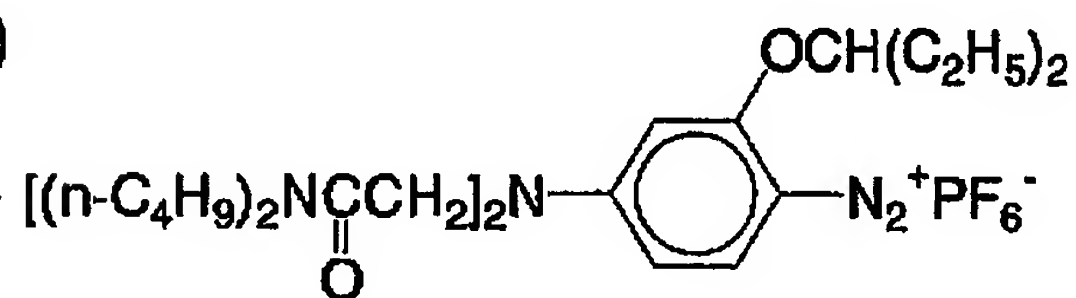
(A-2)



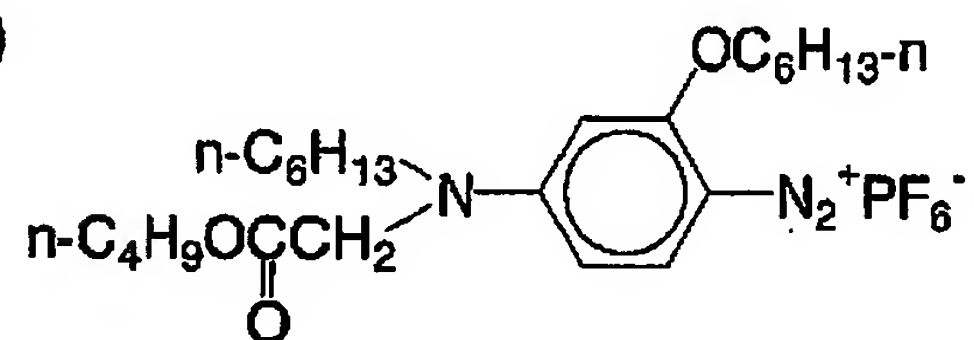
(A-3)



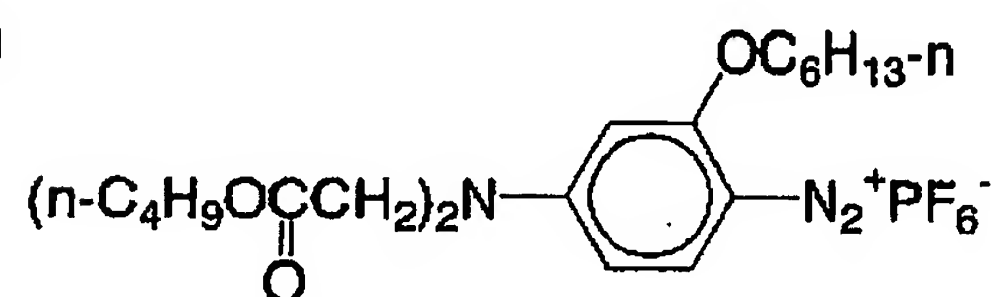
(A-4)



(A-5)

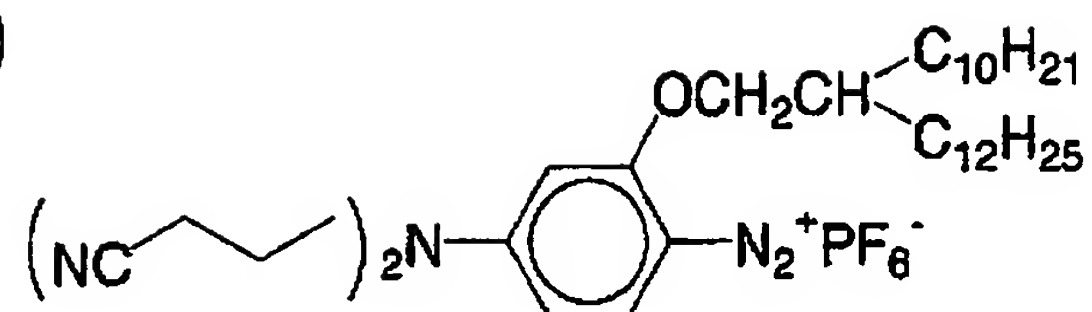


(A-6)

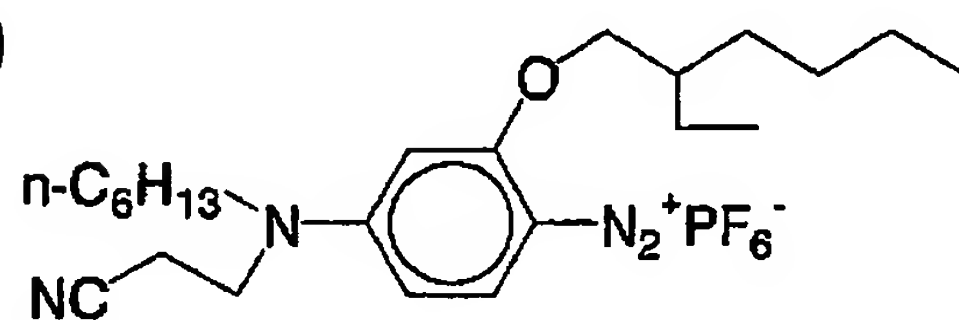


[0050]

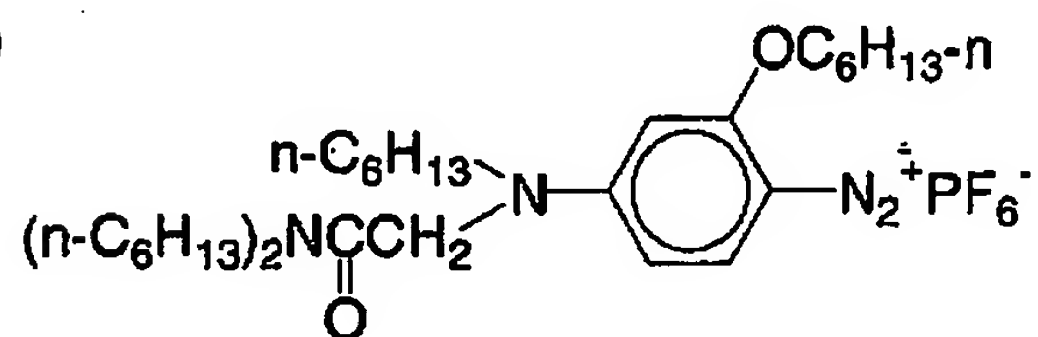
(A-7)



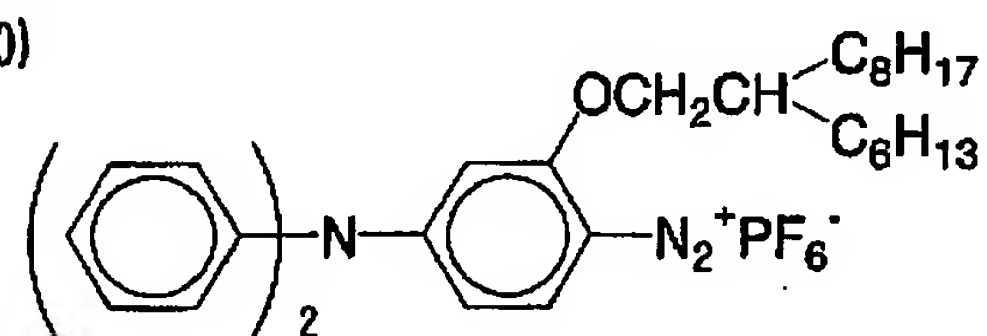
(A-8)



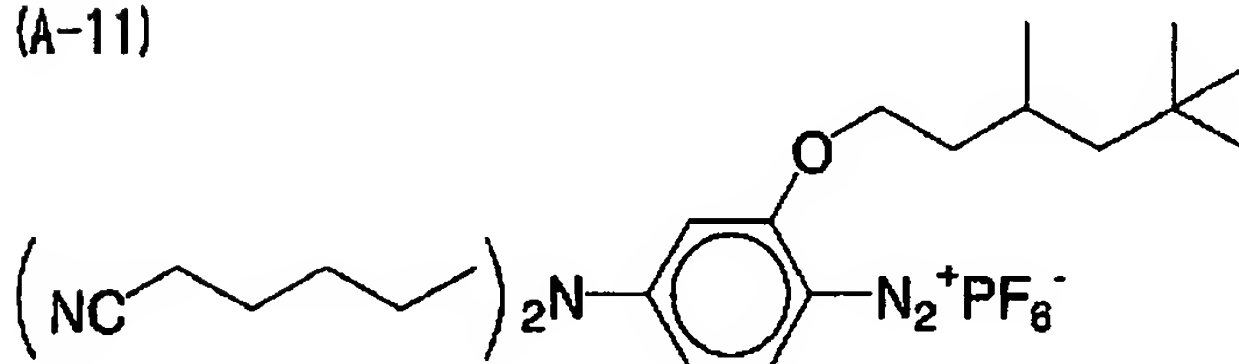
(A-9)



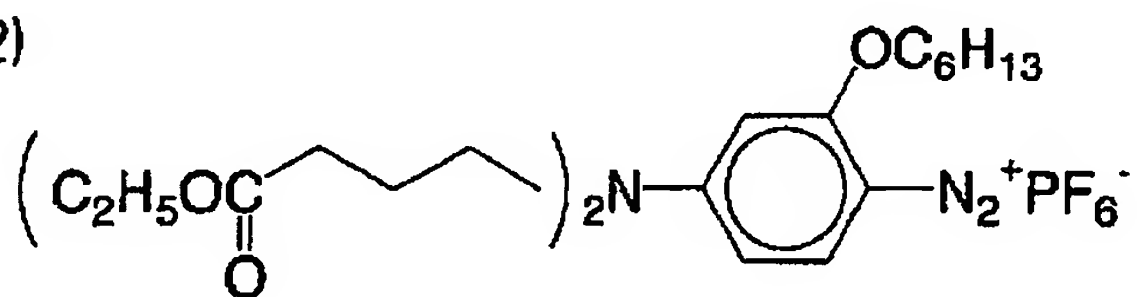
(A-10)



(A-11)

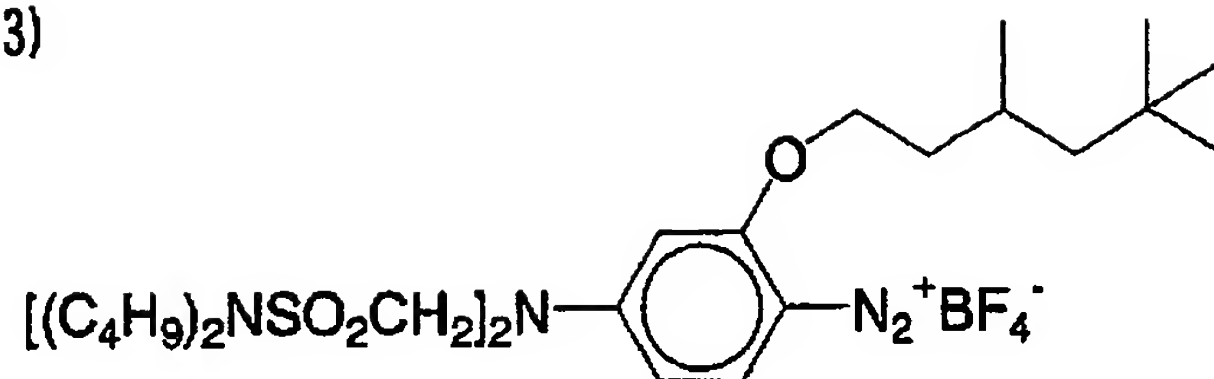


(A-12)

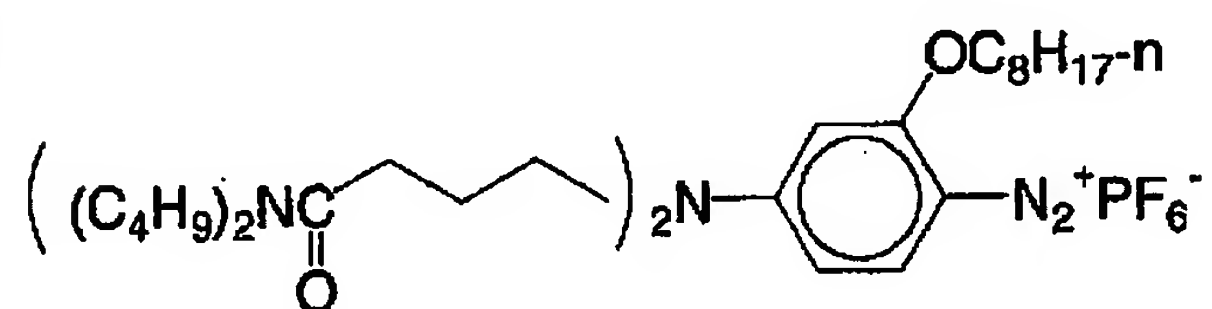


[0051]

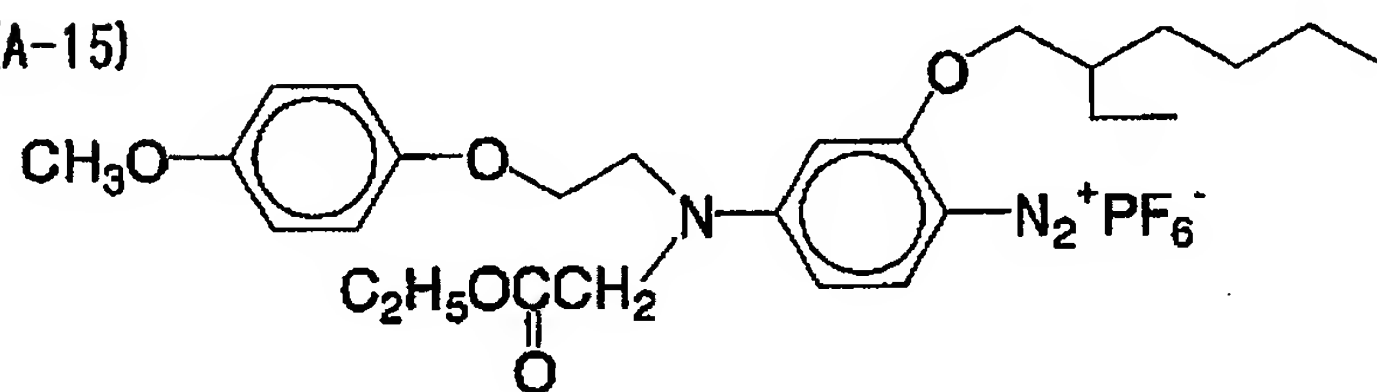
(A-13)



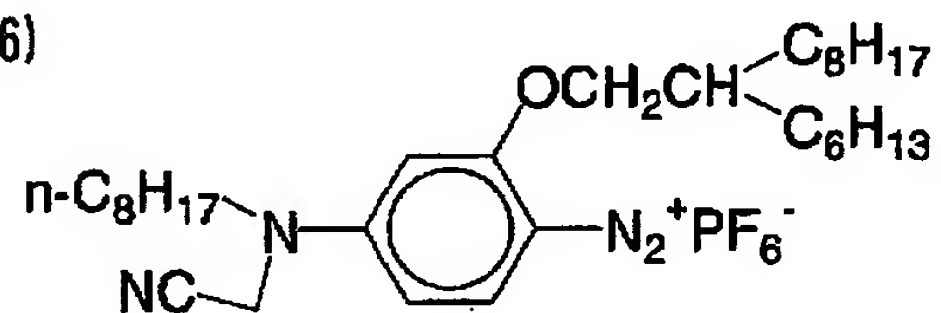
(A-14)



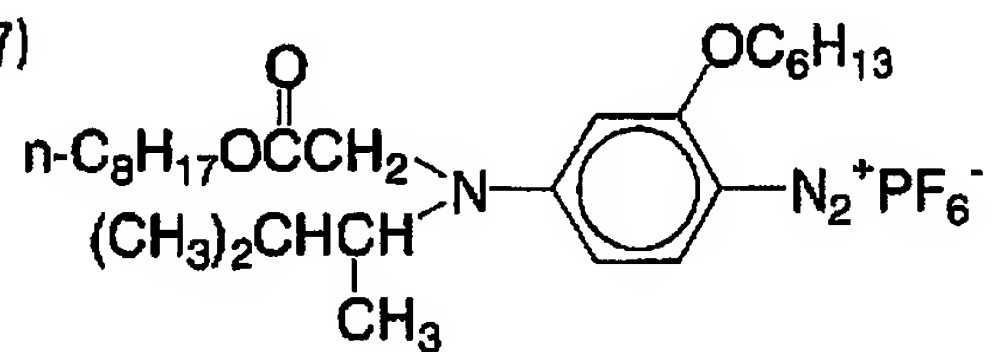
(A-15)



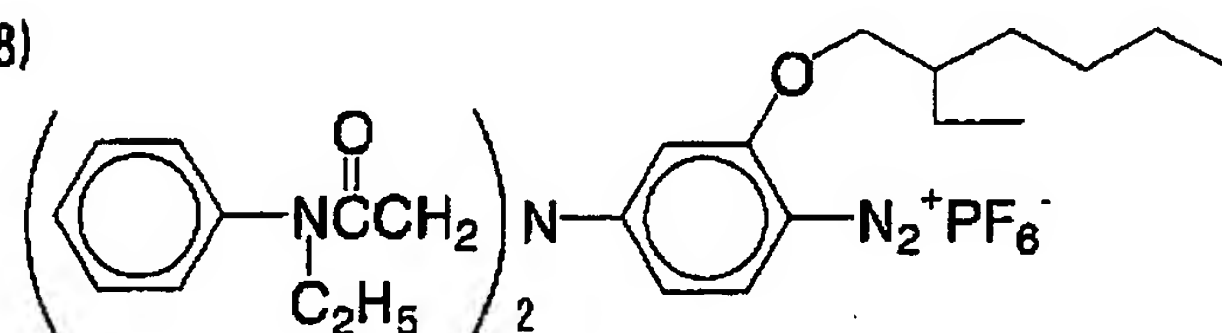
(A-16)



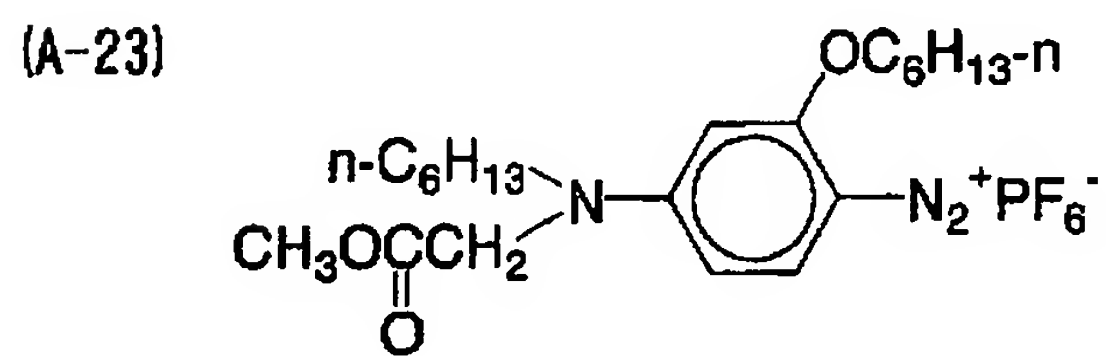
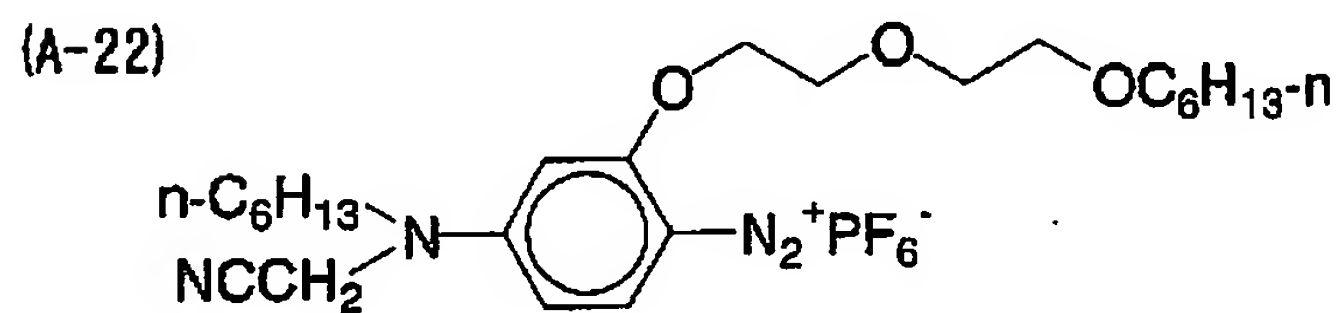
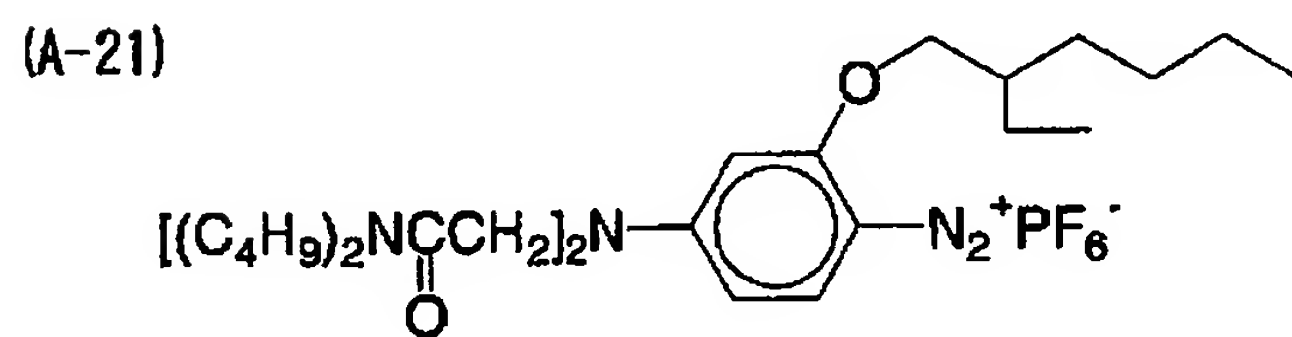
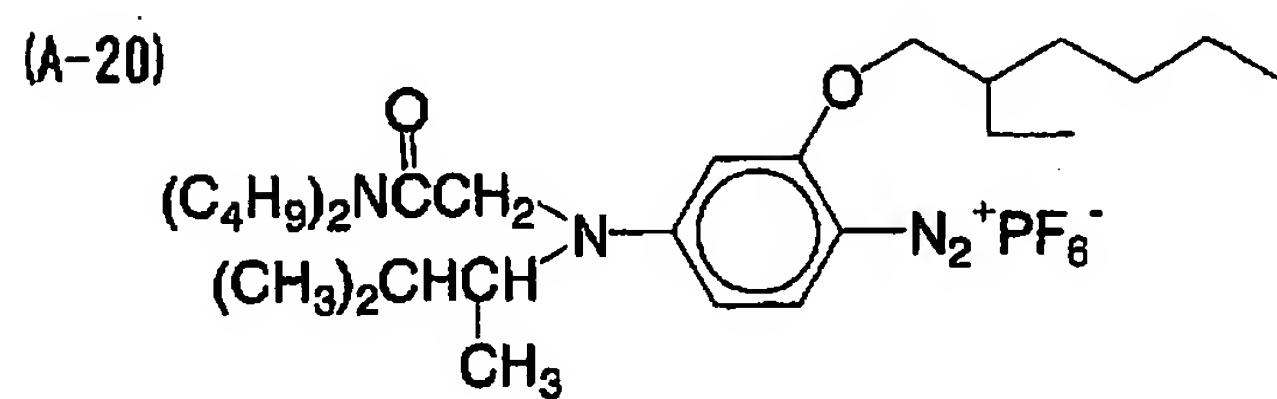
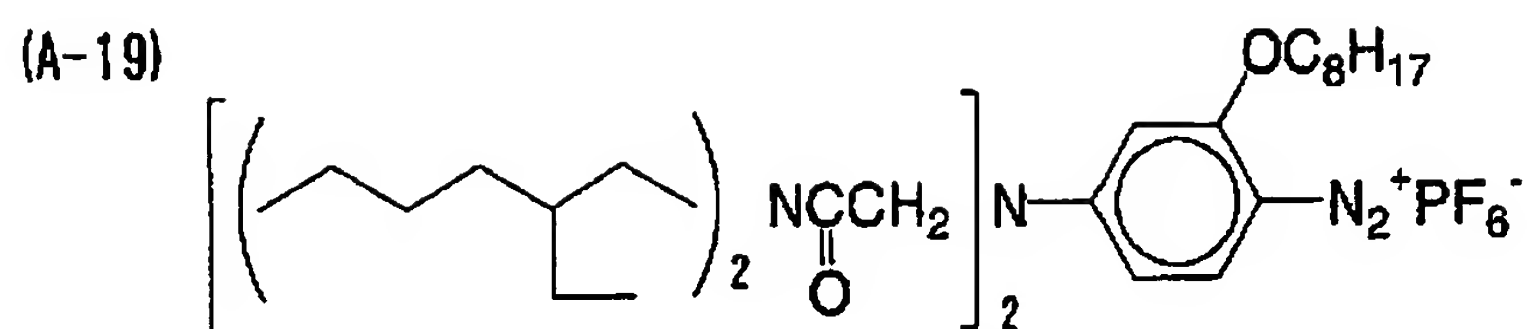
(A-17)



(A-18)

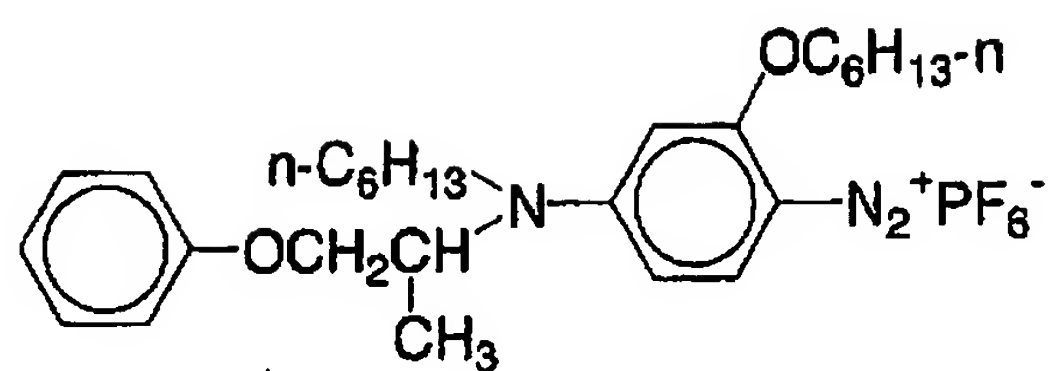


[0052]

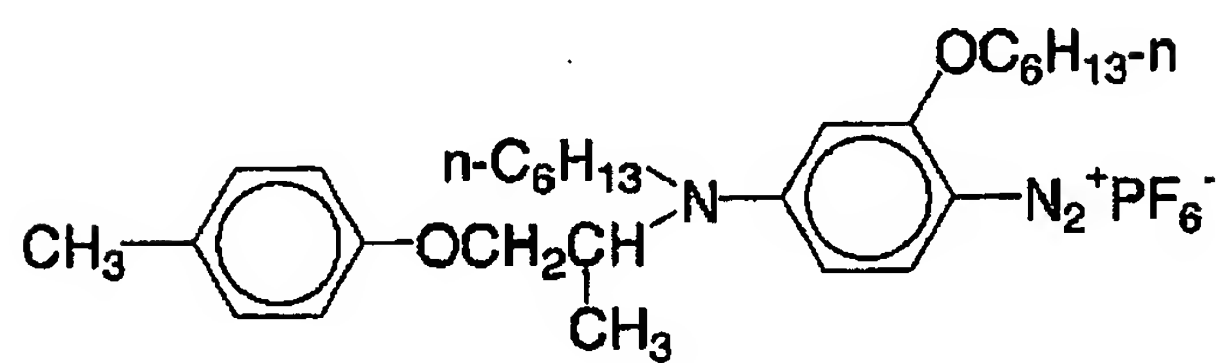


[0053]

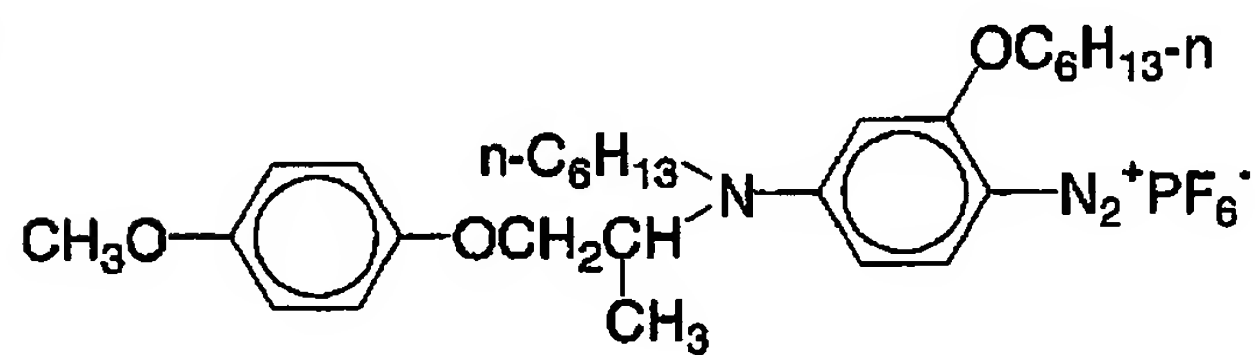
(A)



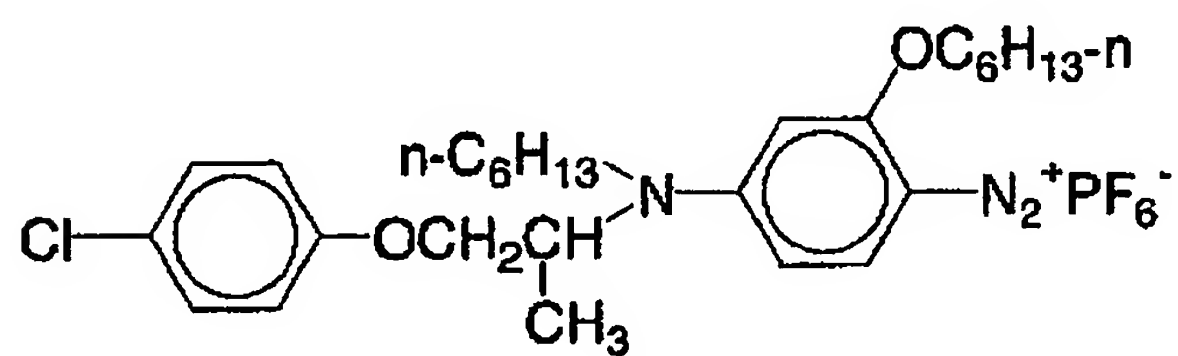
(B)



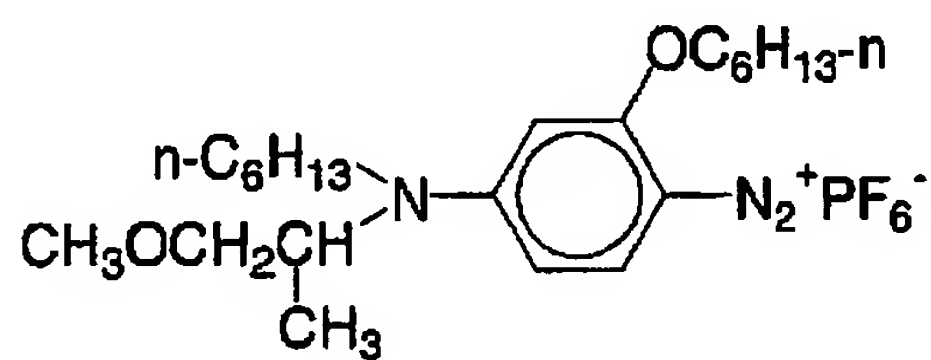
(C)



(D)

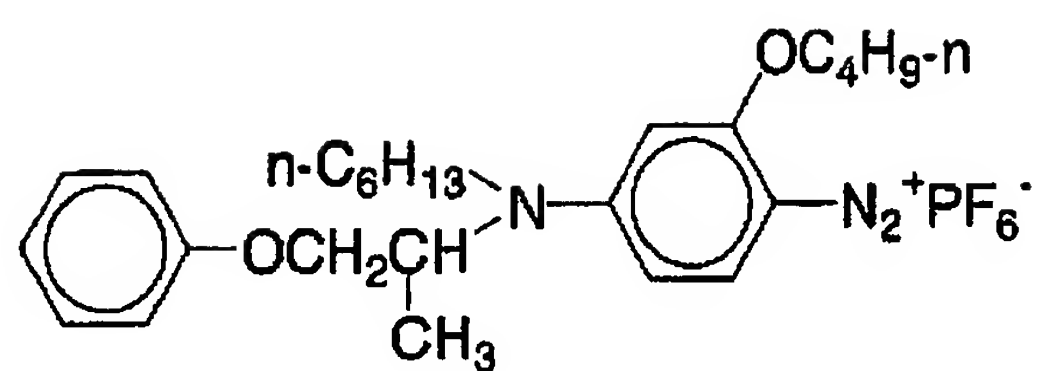


(E)

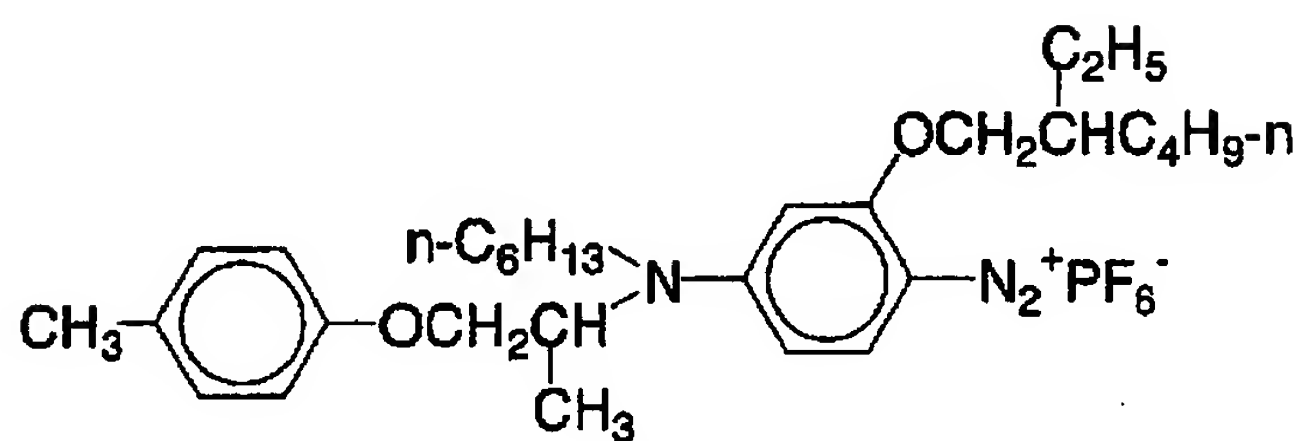


[0054]

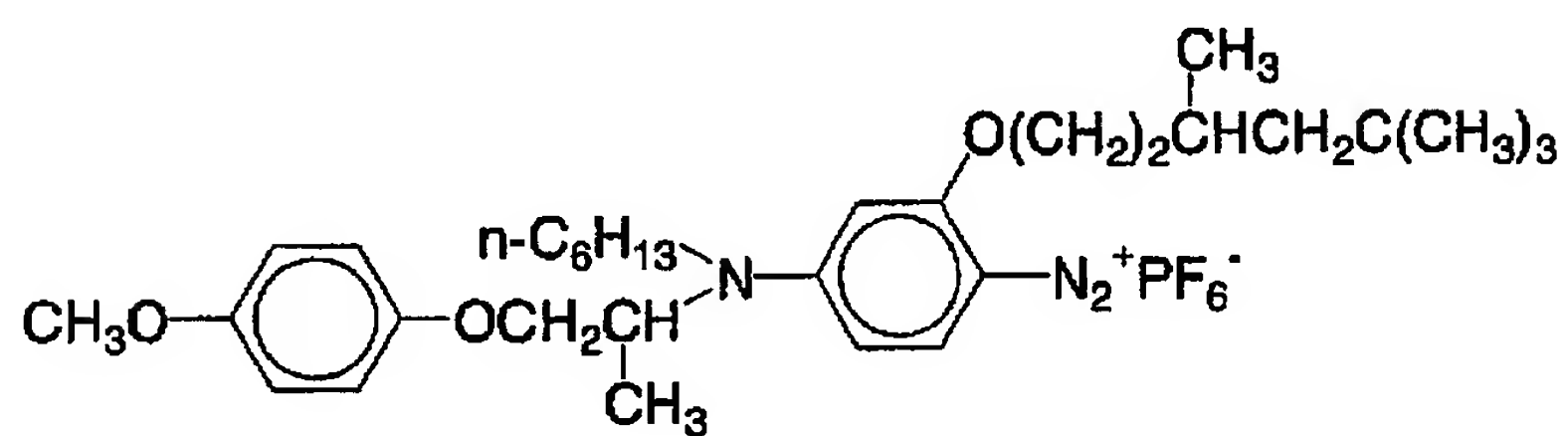
(F)



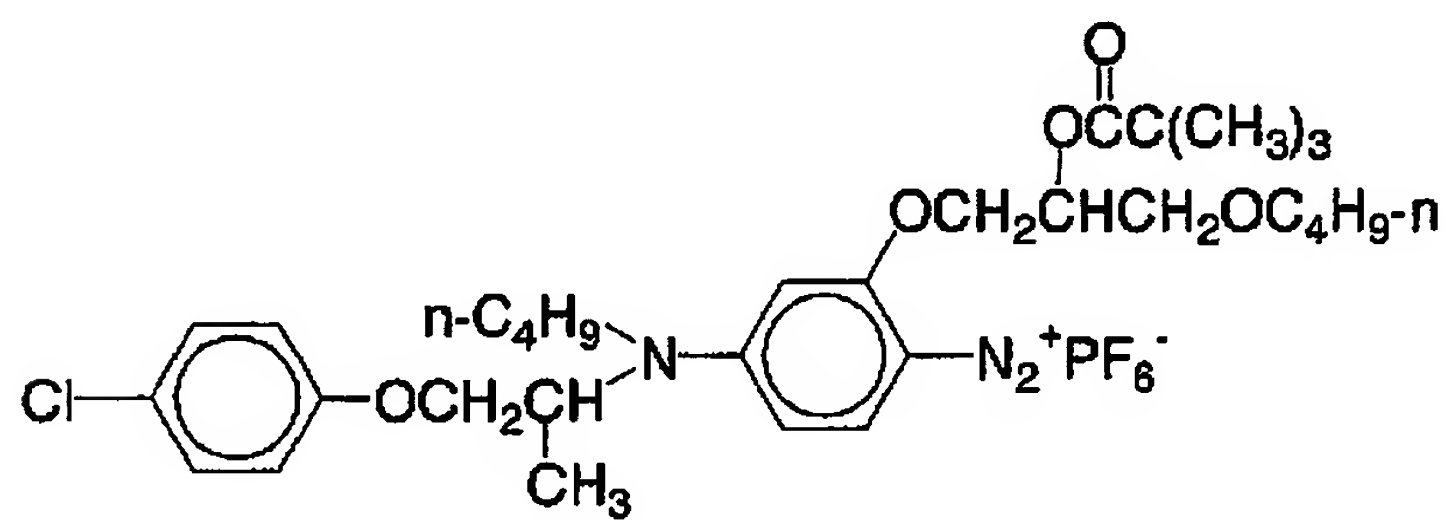
(G)



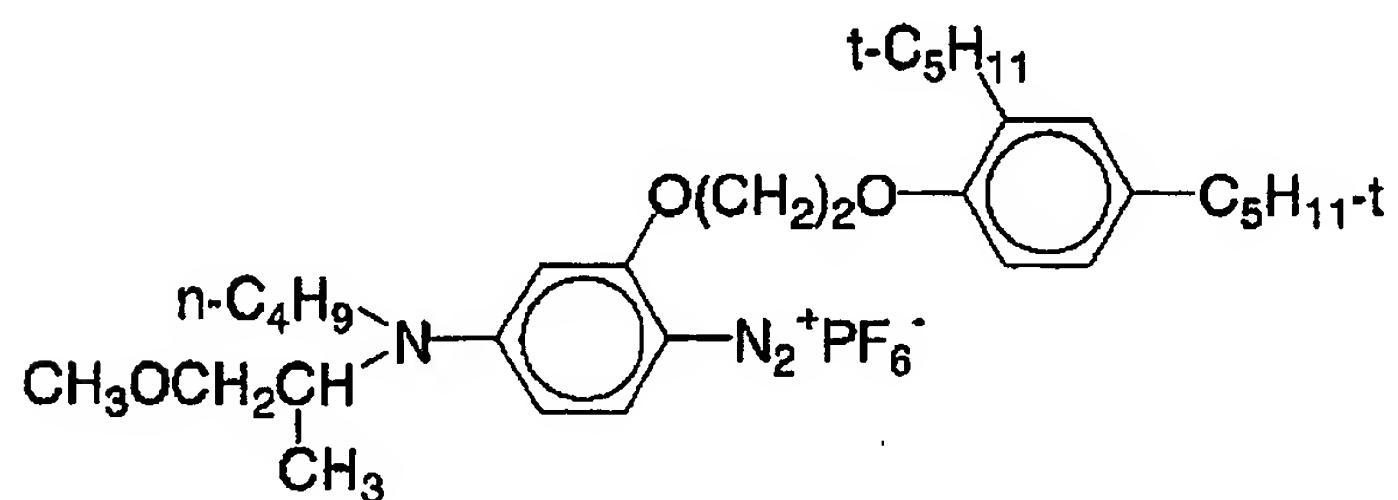
(H)



(I)

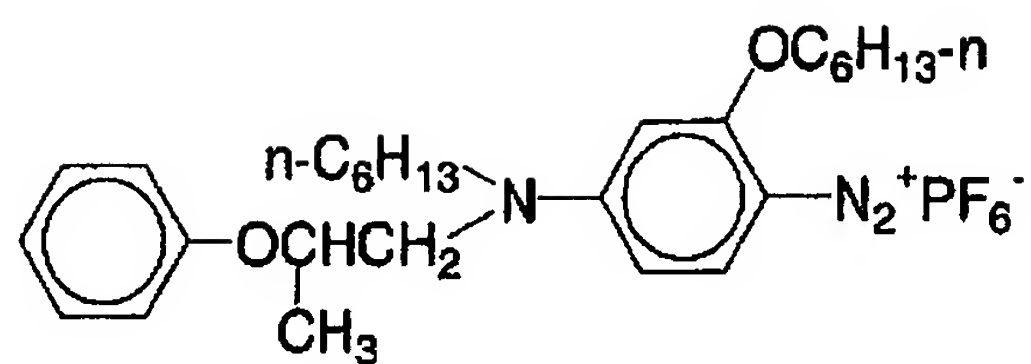


(J)

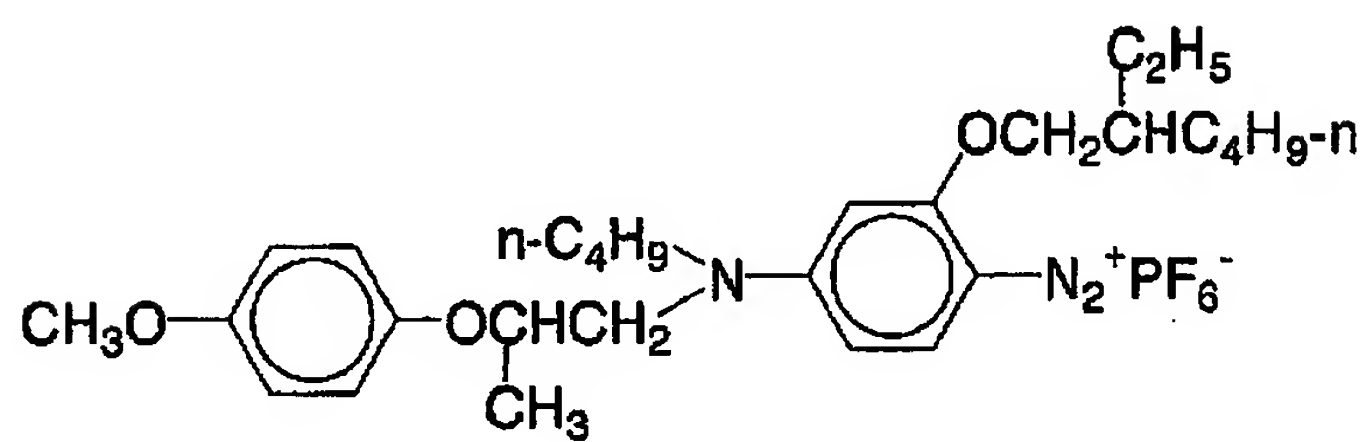


[0055]

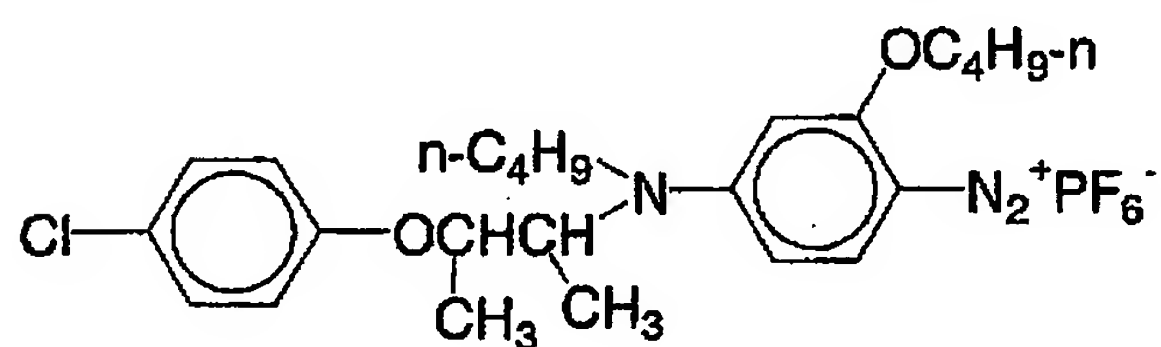
(K)



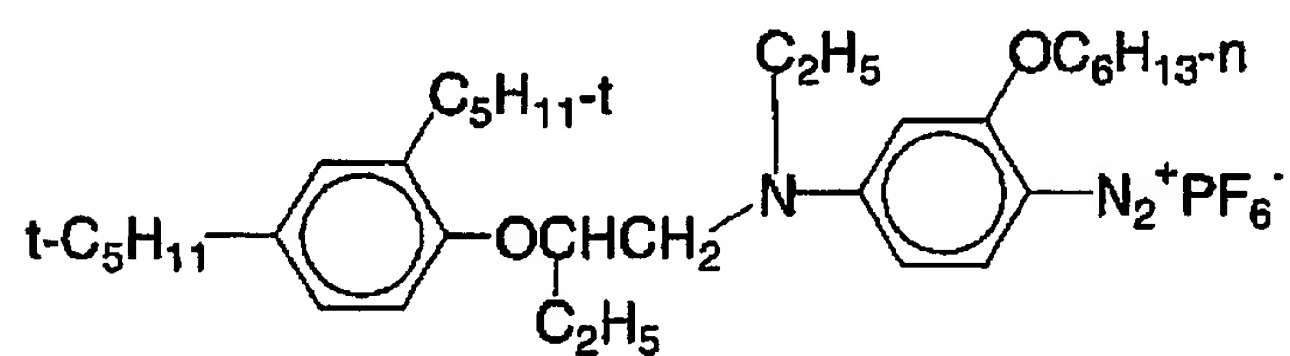
(L)



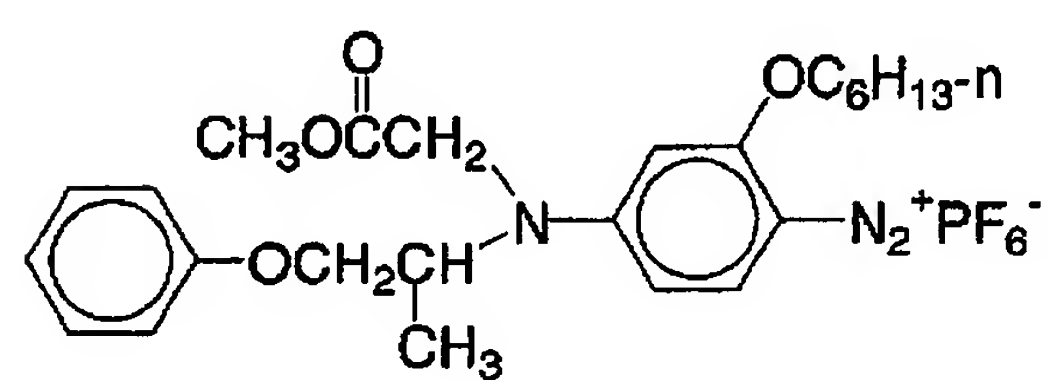
(M)



(N)

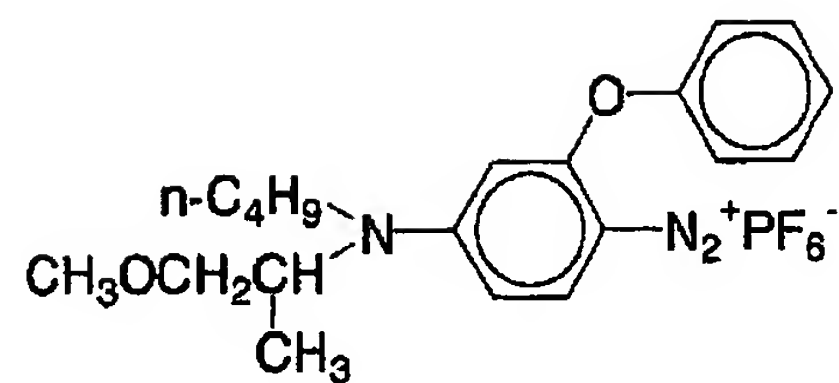


(O)

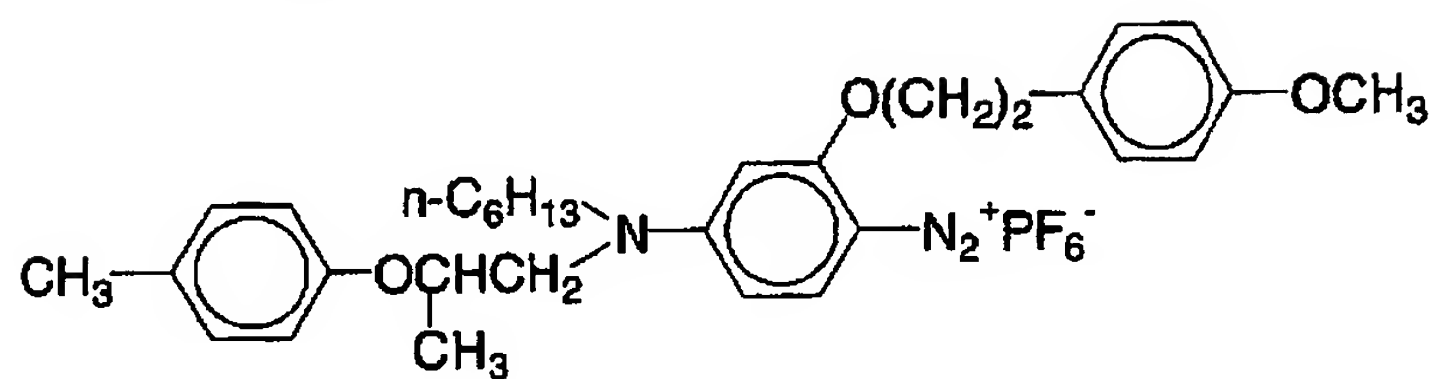


[0056]

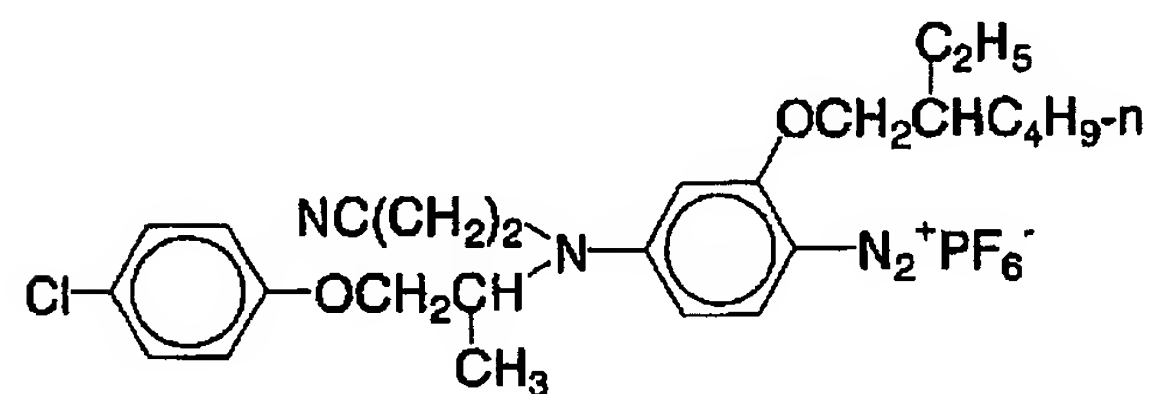
(P)



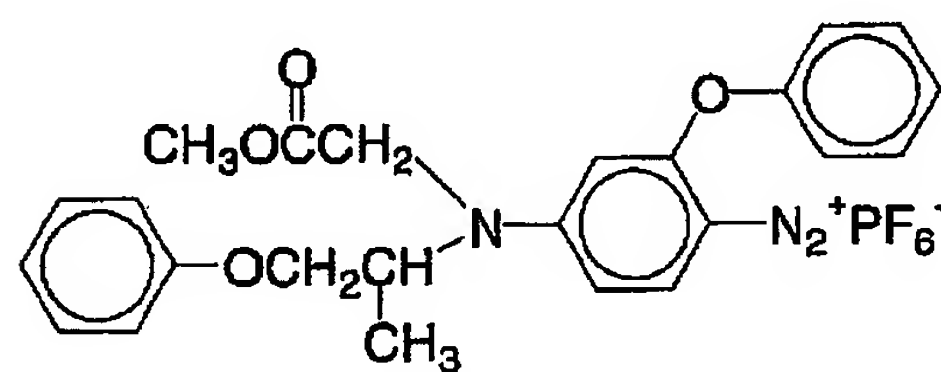
(Q)



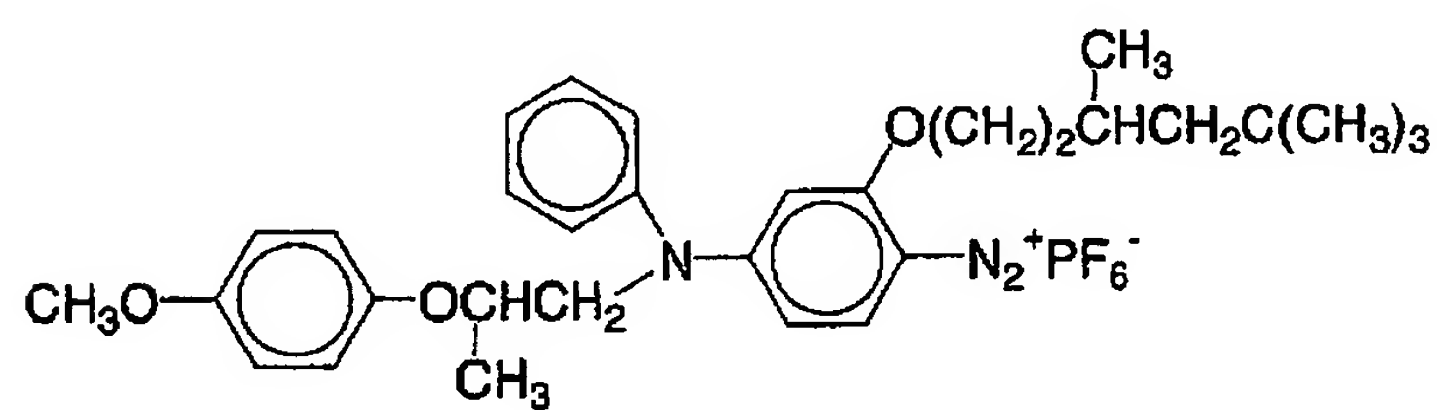
(R)



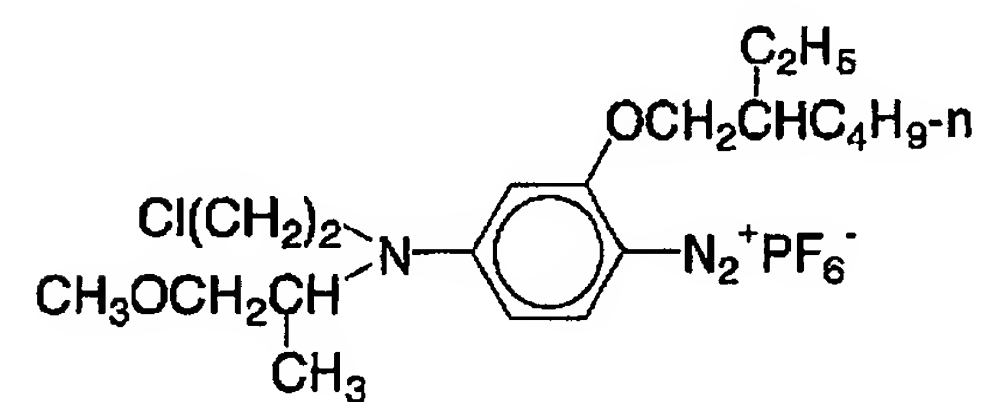
(S)



(T)

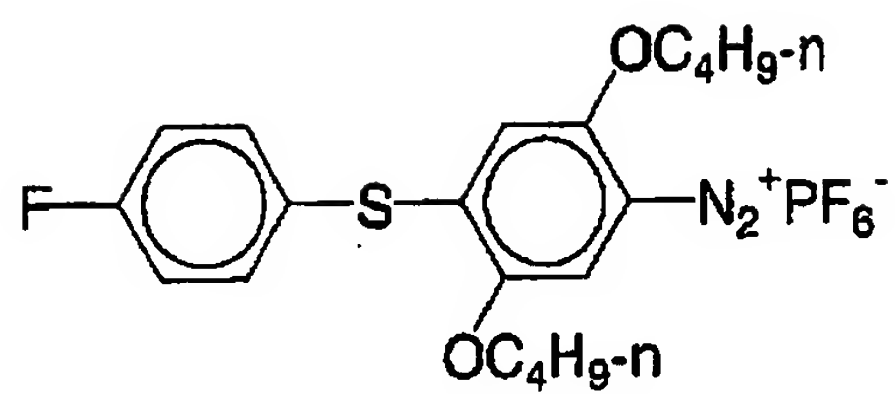


(U)

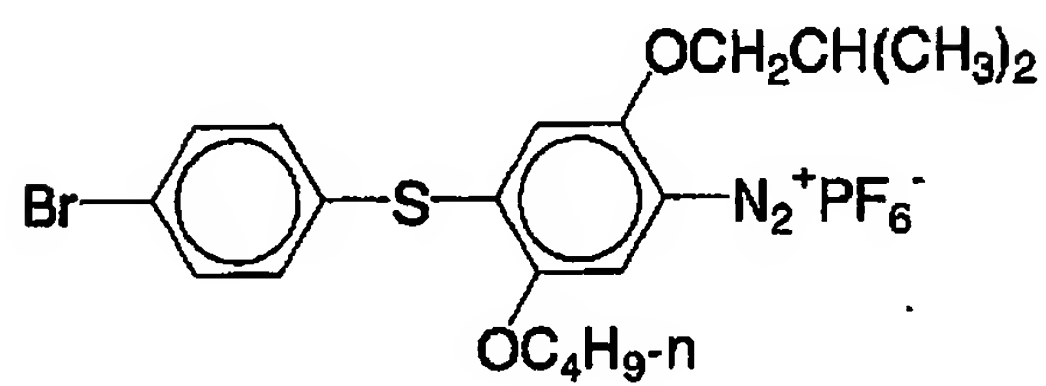


[0057]

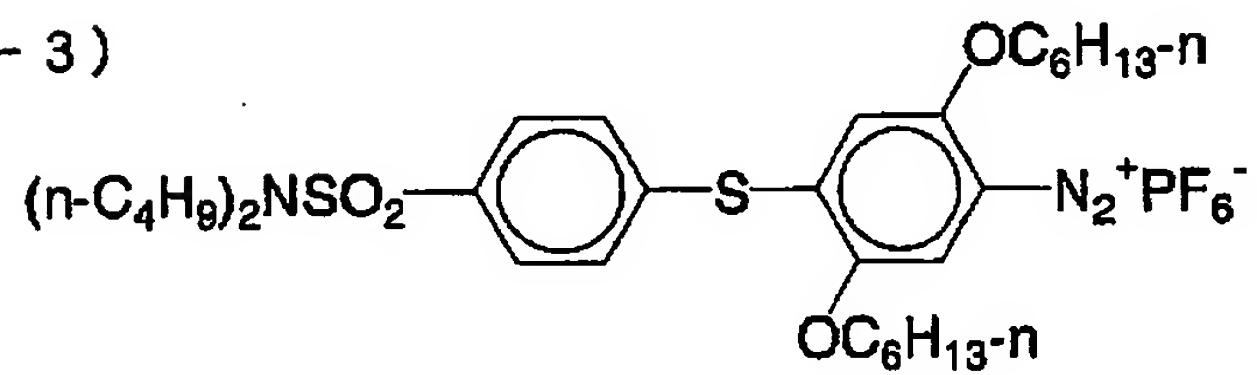
(1-1)



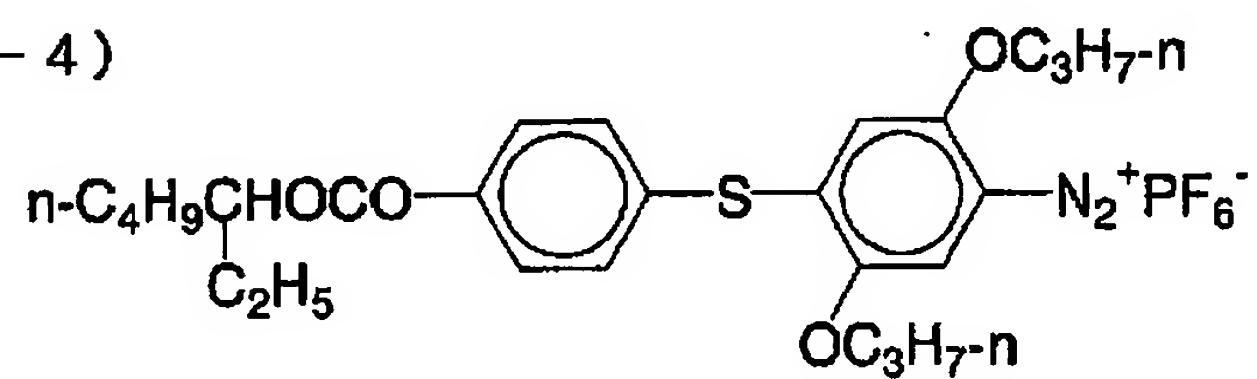
(1-2)



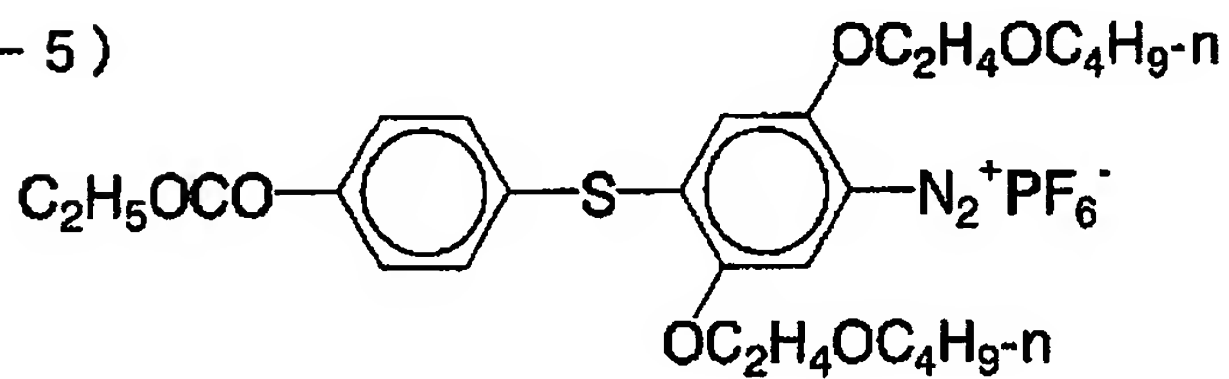
(1-3)



(1-4)

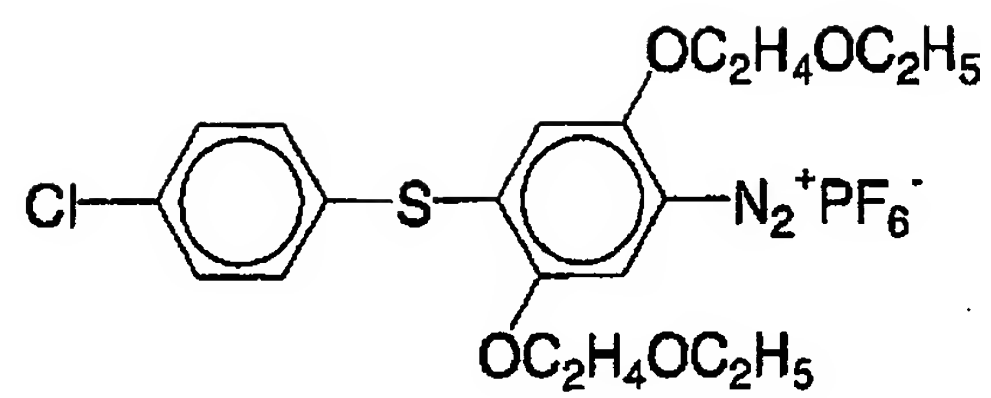


(1-5)

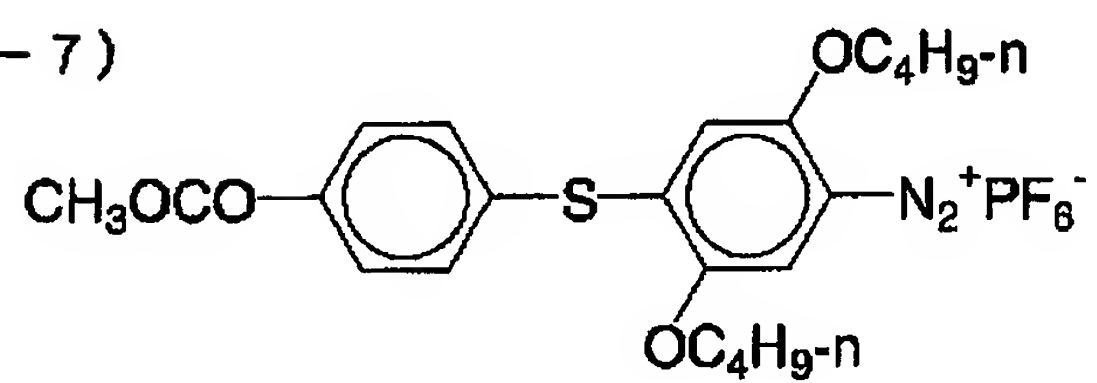


[0058]

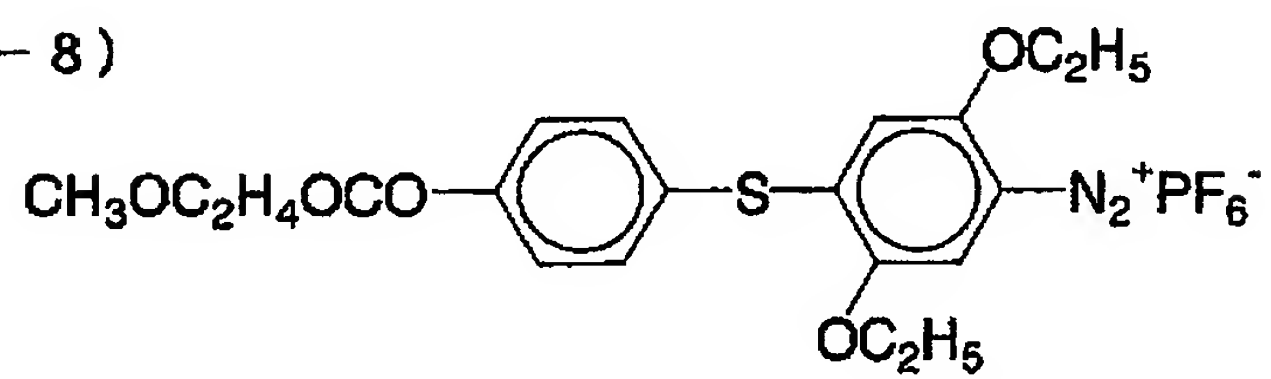
(1-6)



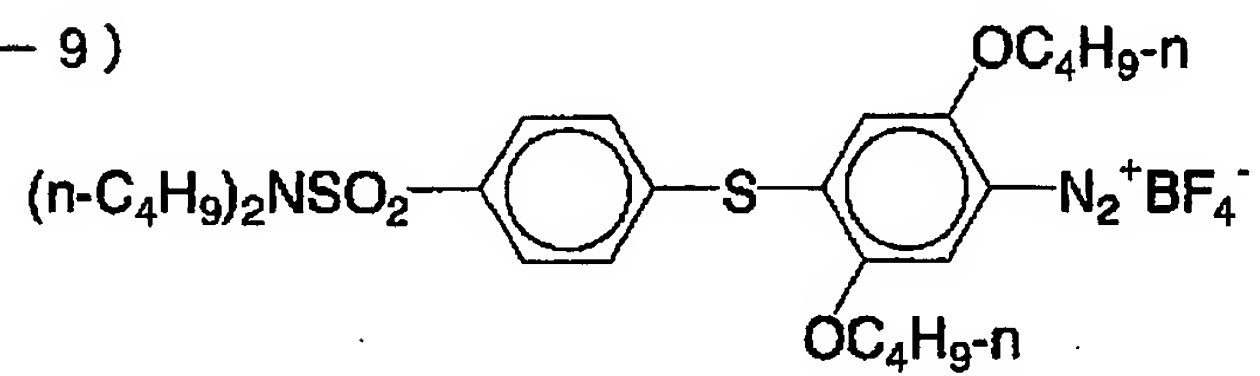
(1-7)



(1-8)

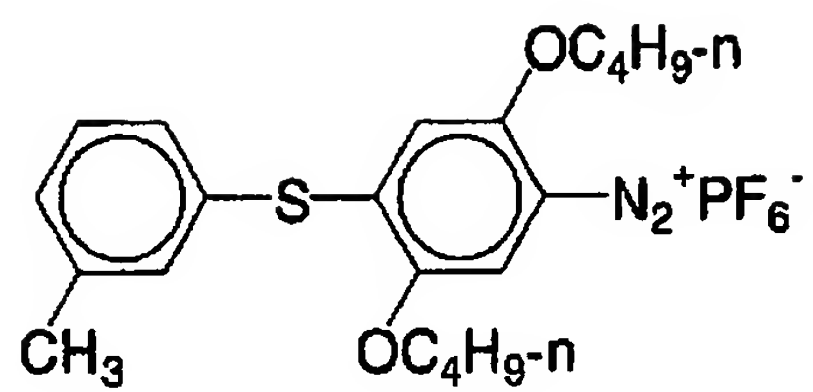


(1-9)

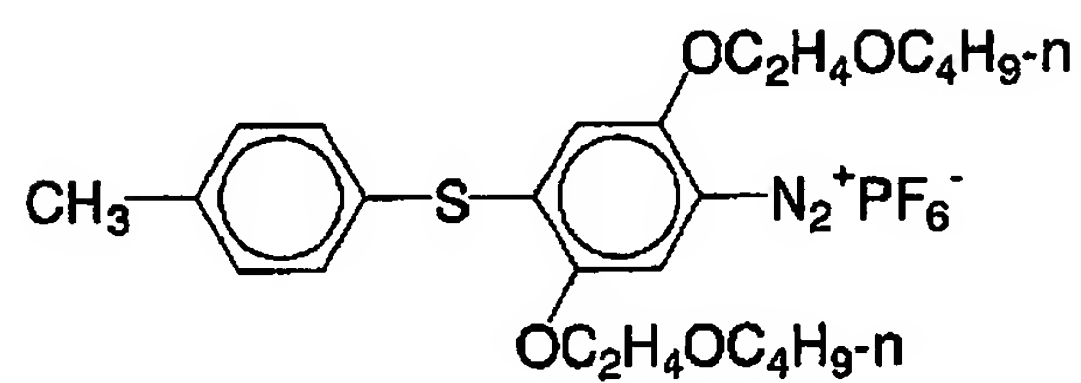


[0059]

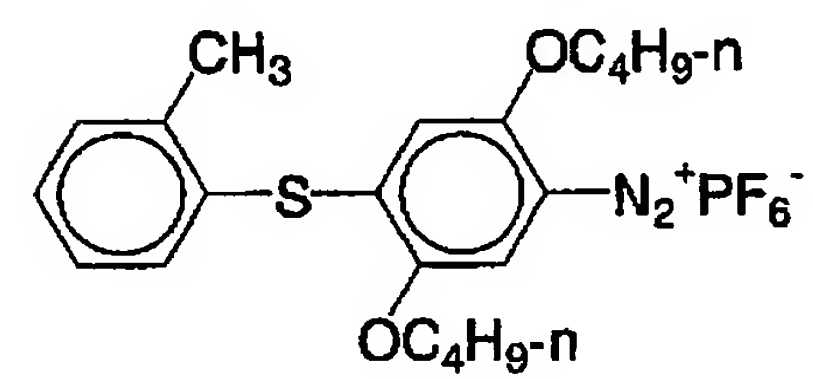
(III-1)



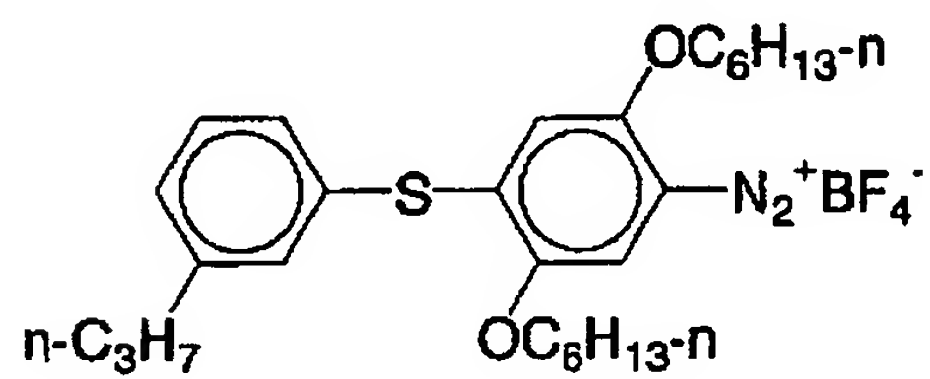
(III-2)



(III-3)

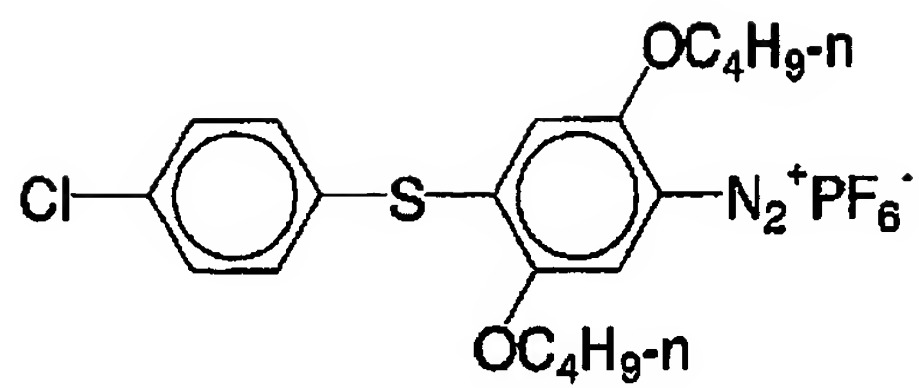


(III-4)

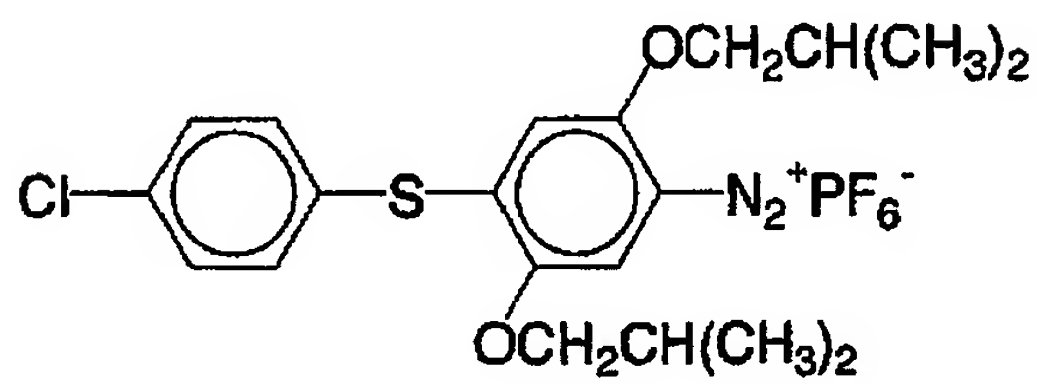


[0060]

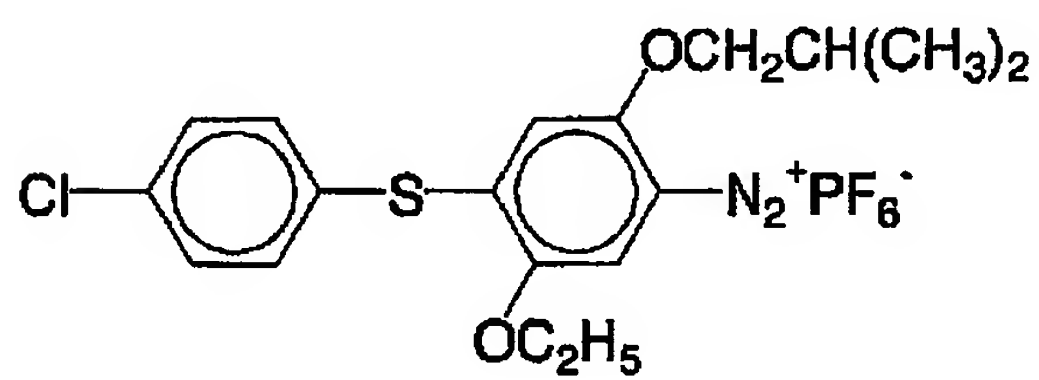
(IV-1)



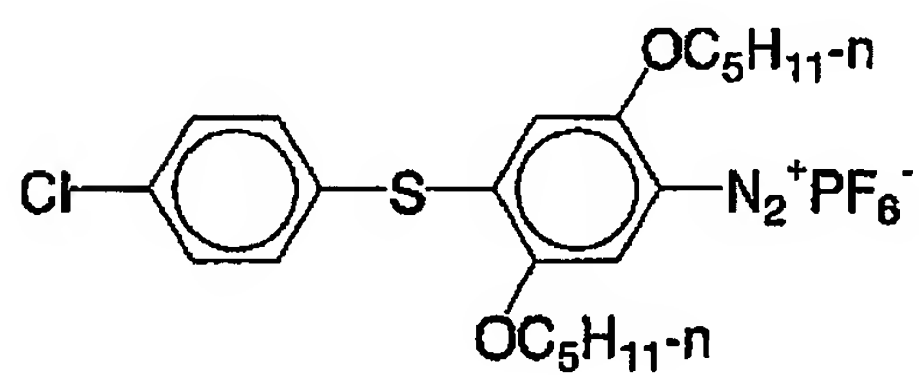
(IV-2)



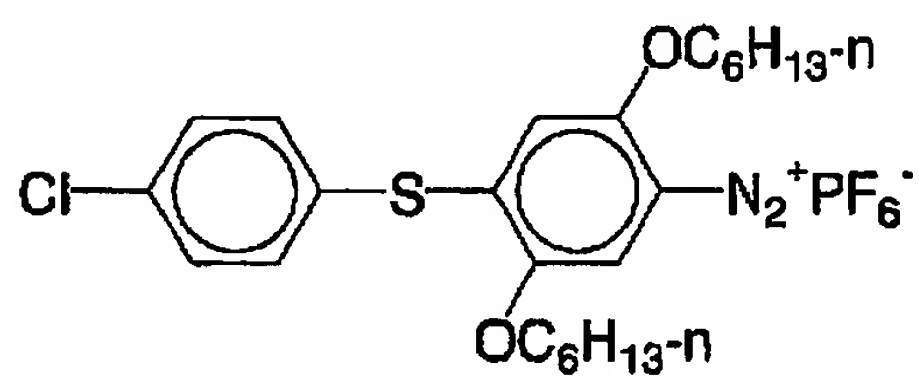
(IV-3)



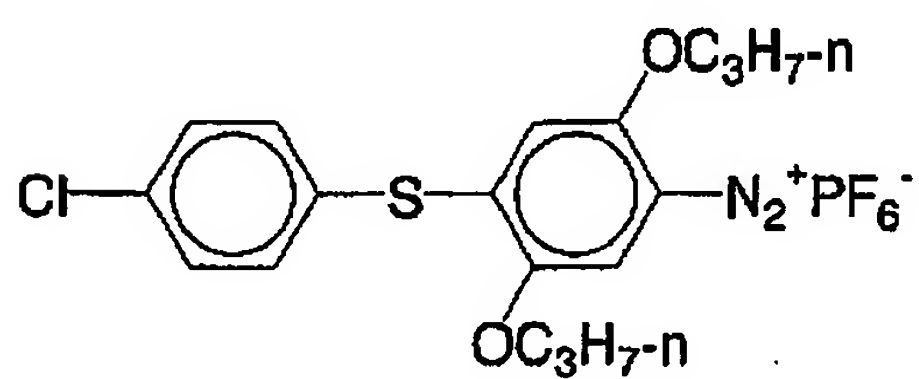
(IV-4)



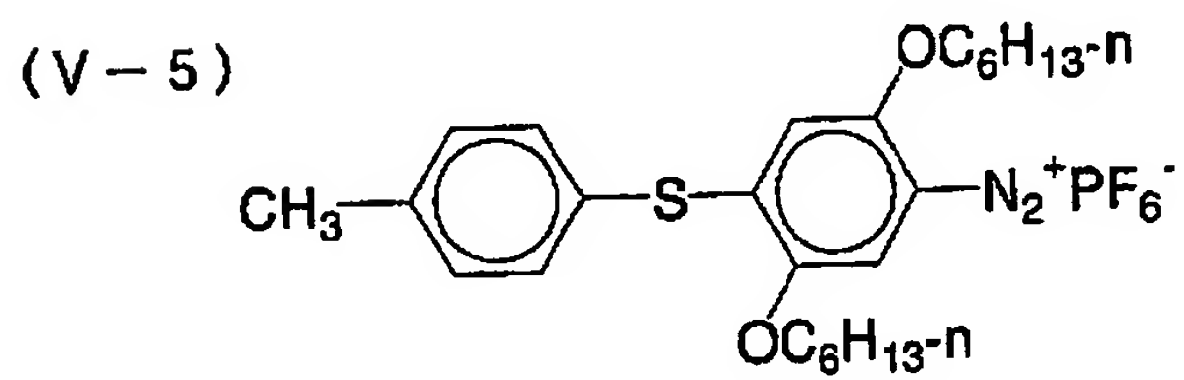
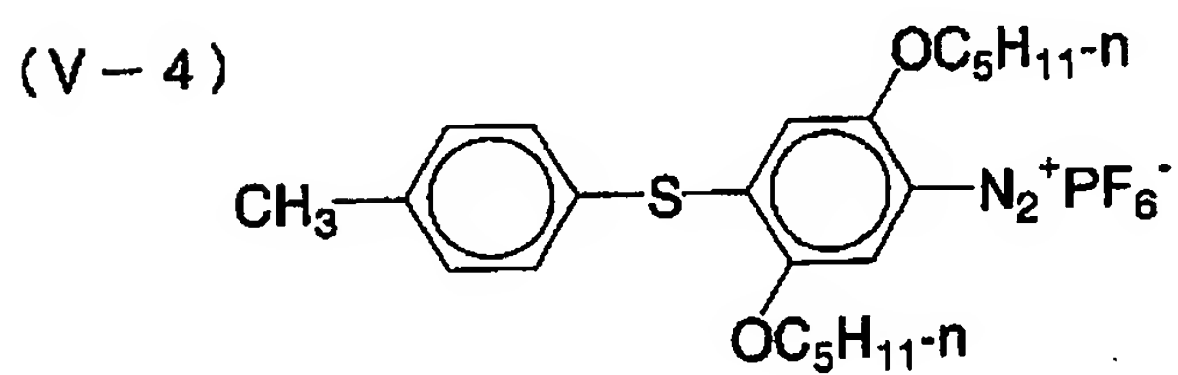
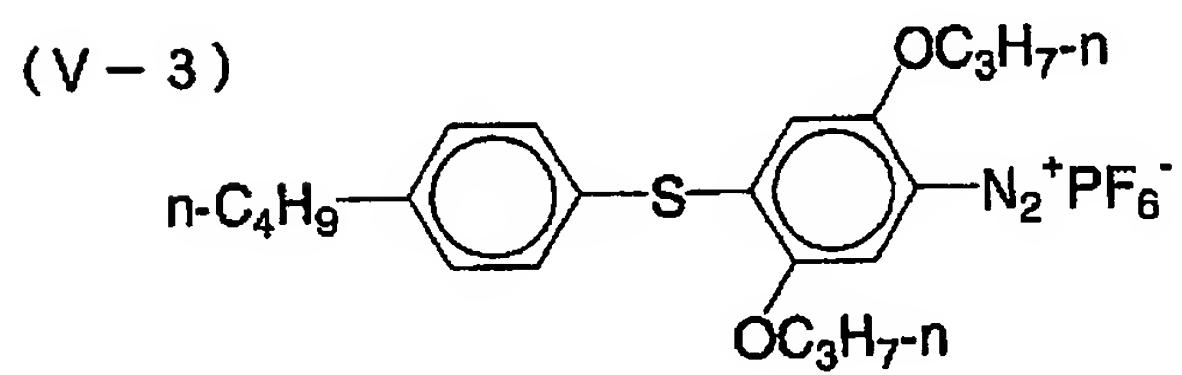
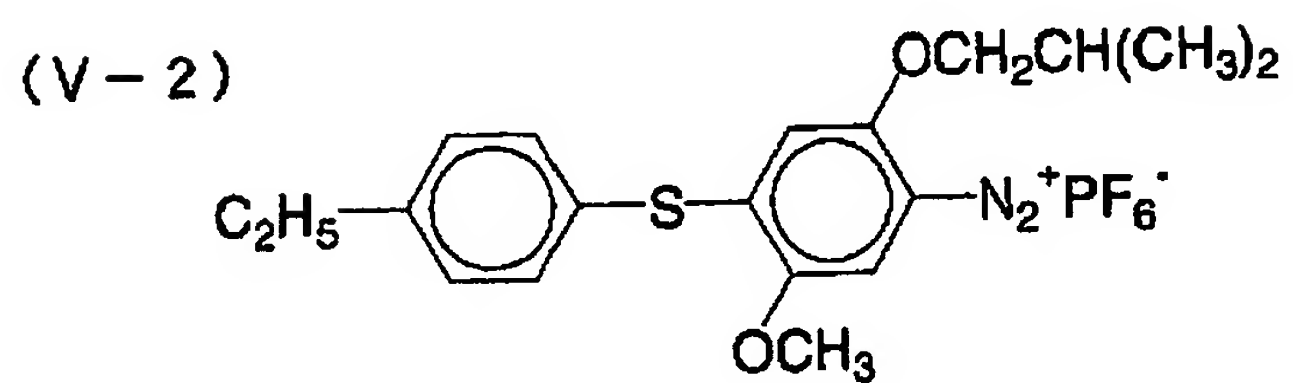
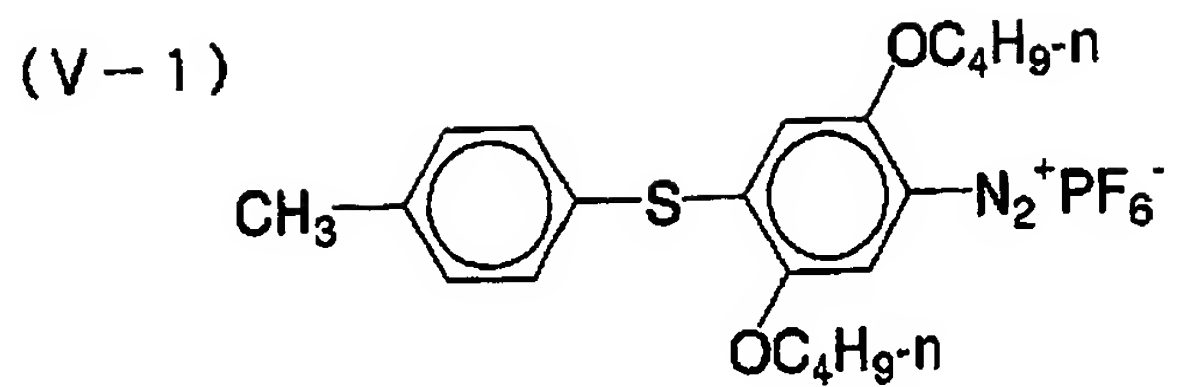
(IV-5)



(IV-6)



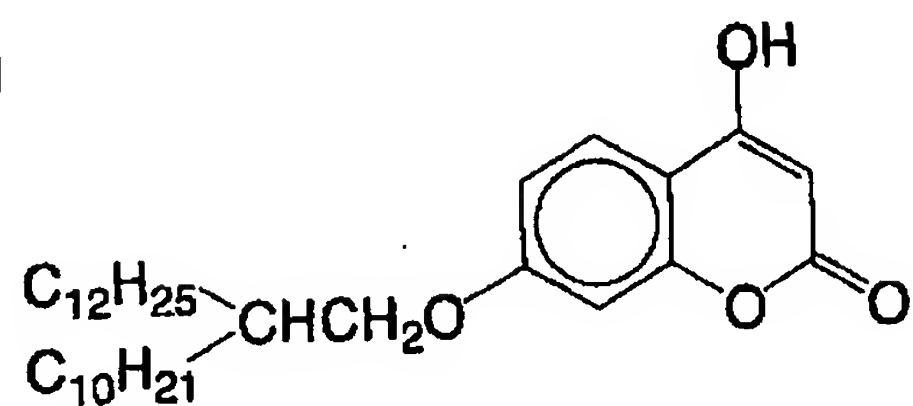
[0061]



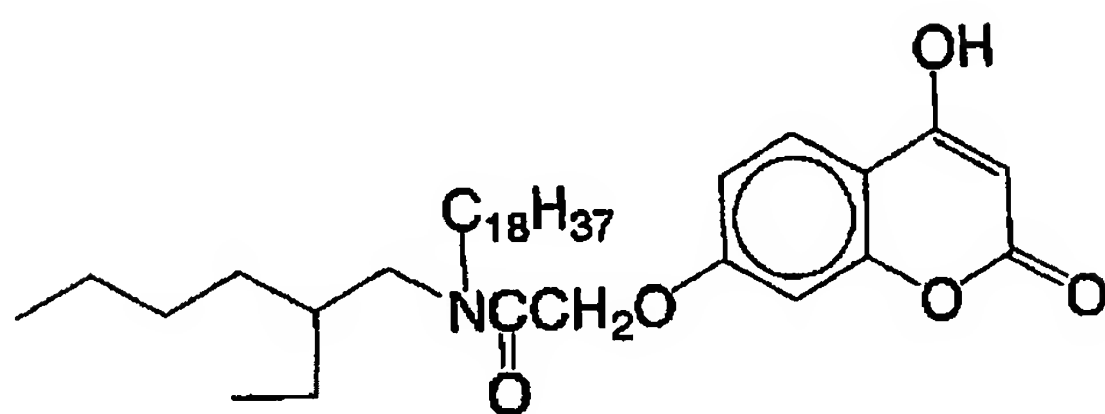
[0062]

-Specific examples of coupler compounds-

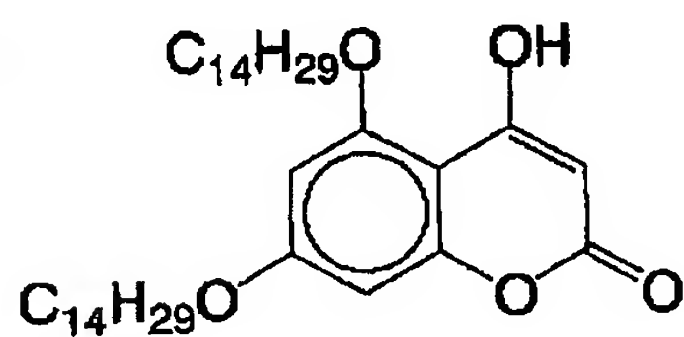
(B-1)



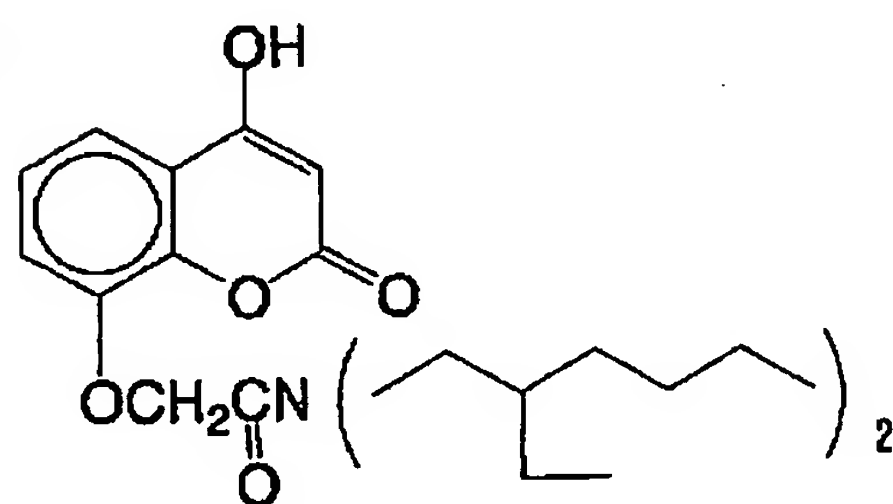
(B-2)



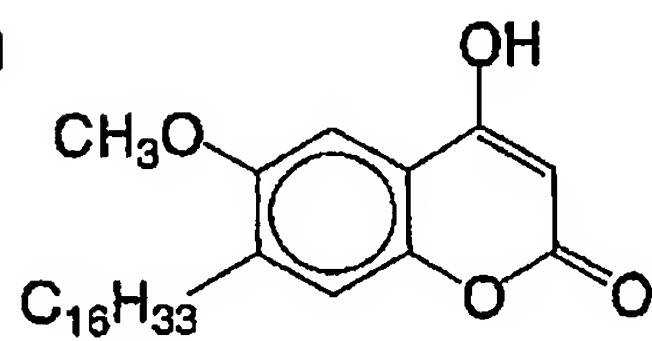
(B-3)



(B-4)

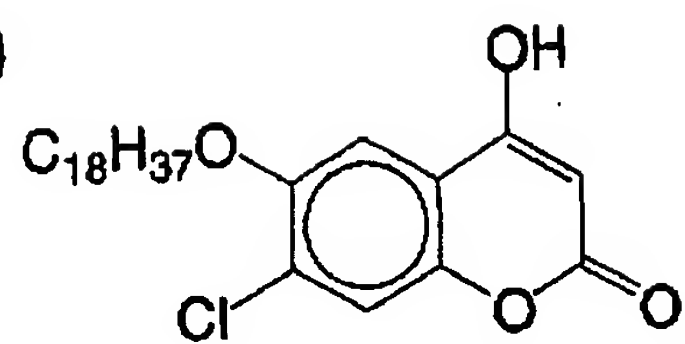


(B-5)

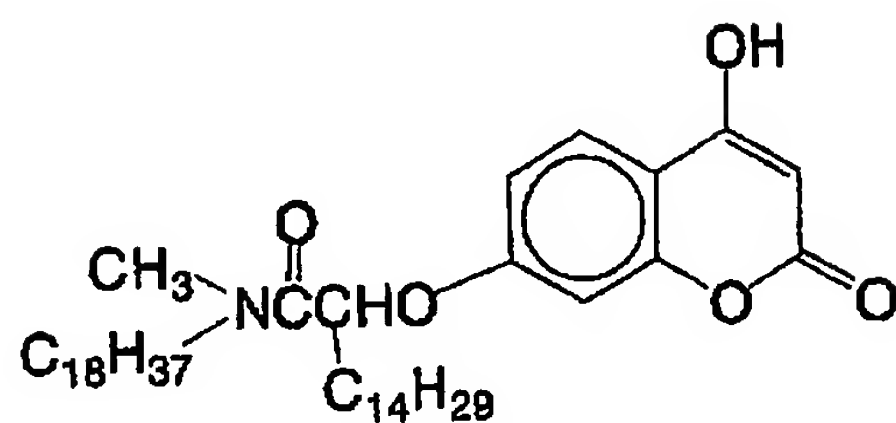


[0063]

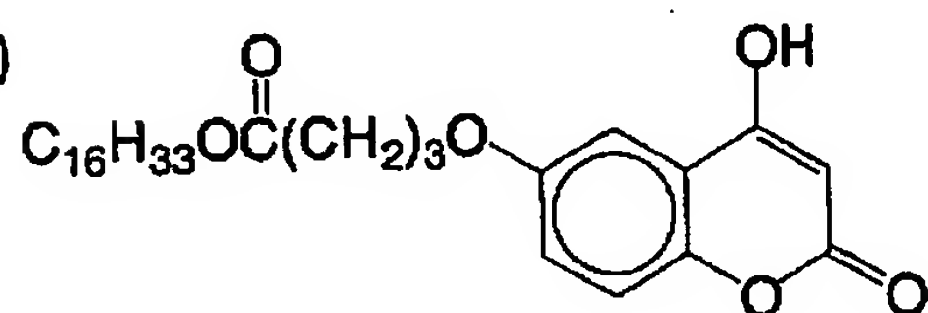
(B-6)



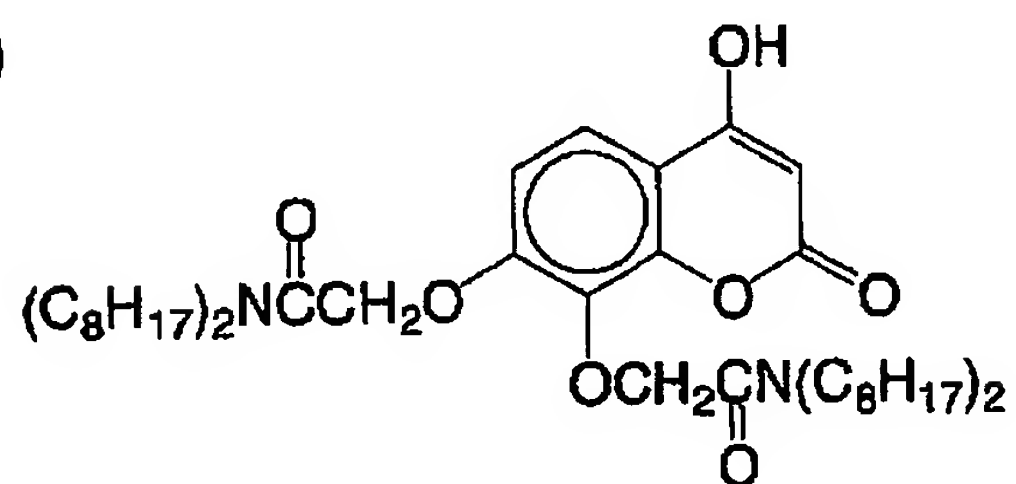
(B-7)



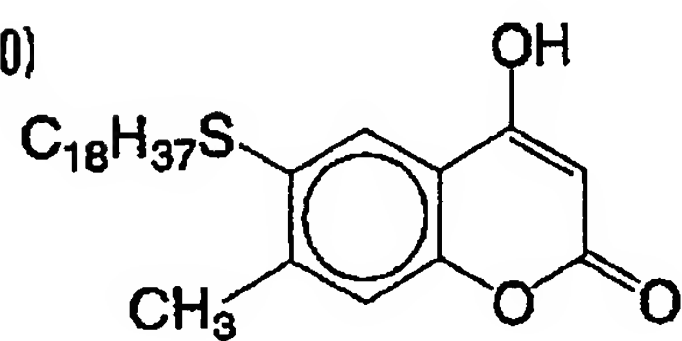
(B-8)



(B-9)

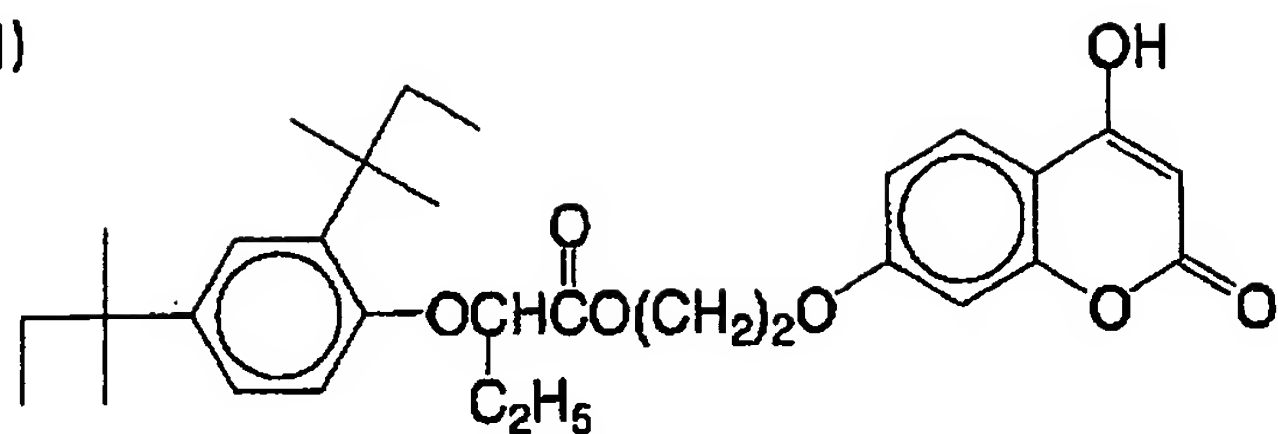


(B-10)

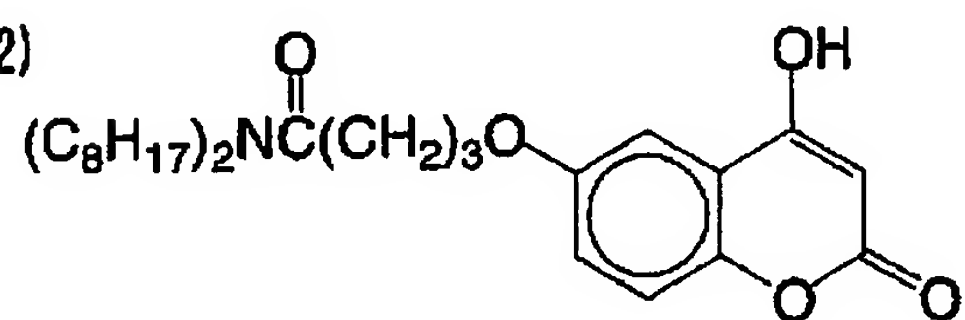


[0064]

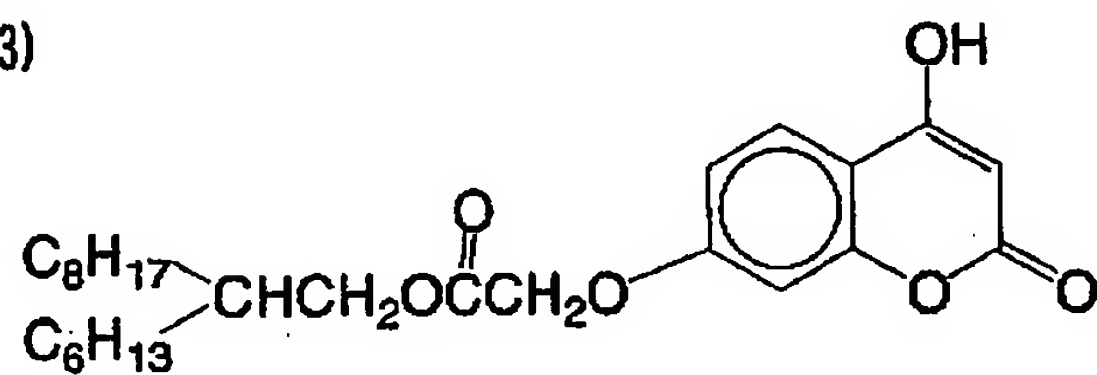
(B-11)



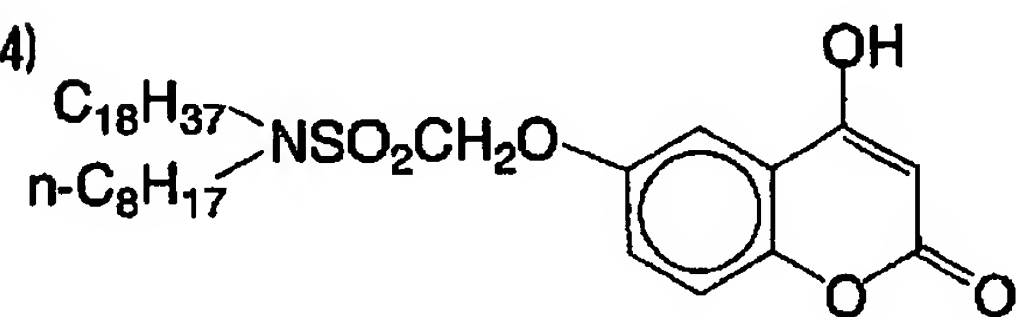
(B-12)



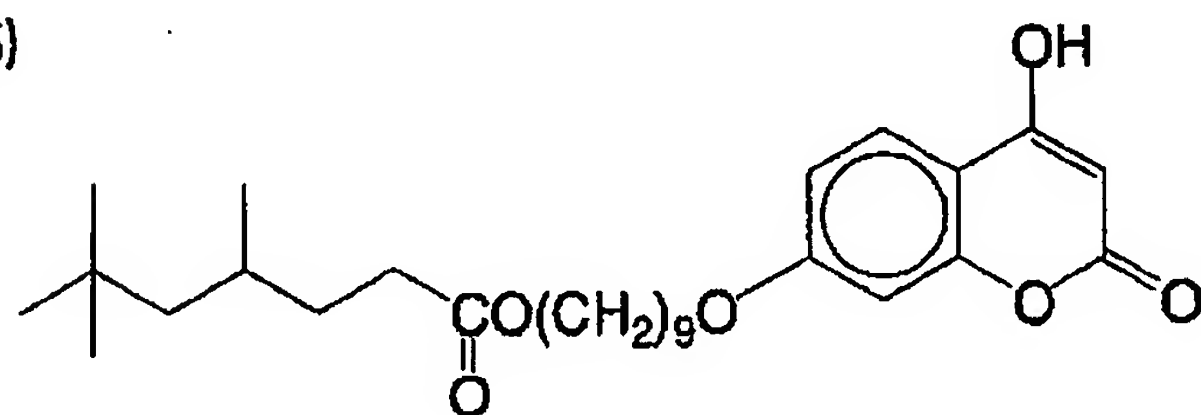
(B-13)



(B-14)

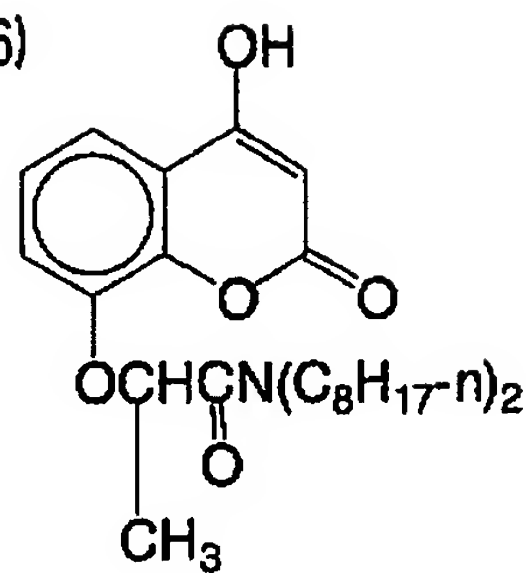


(B-15)

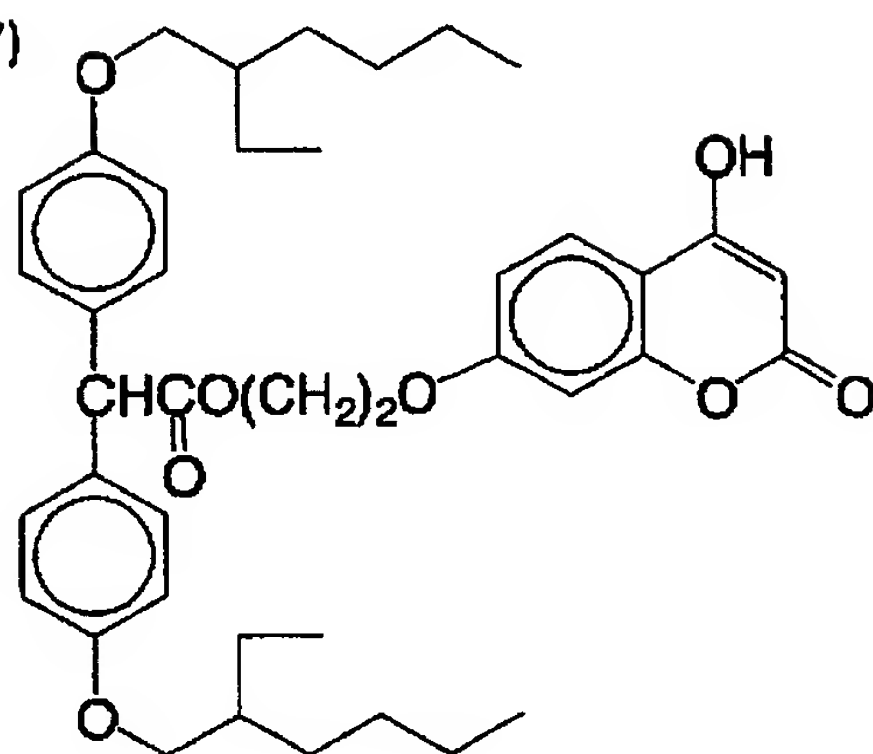


[0065]

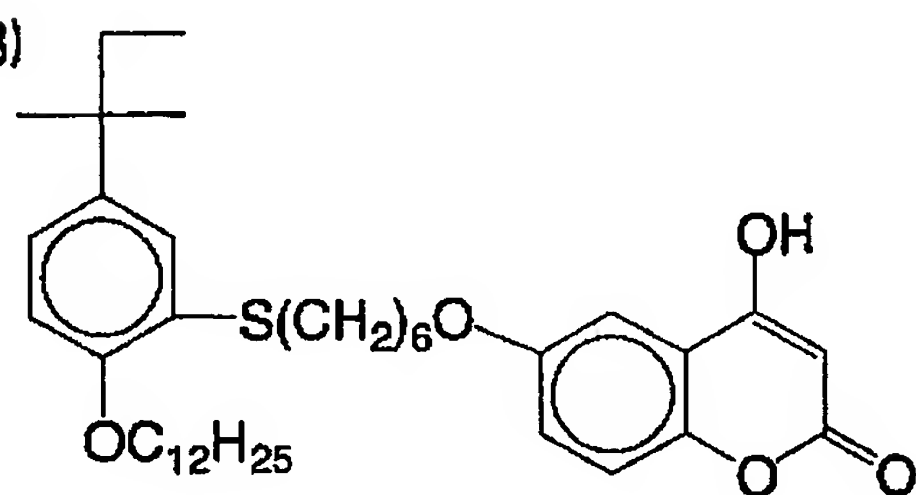
(B-16)



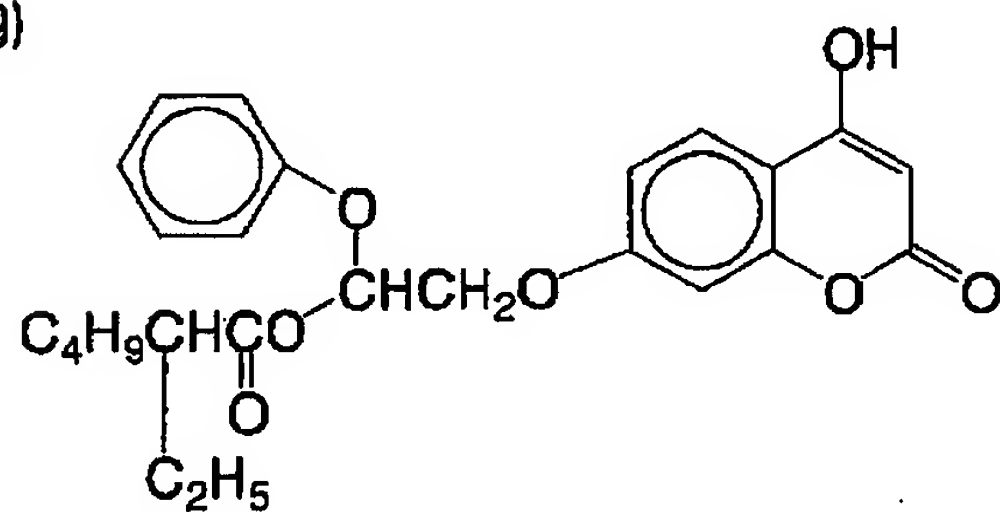
(B-17)



(B-18)

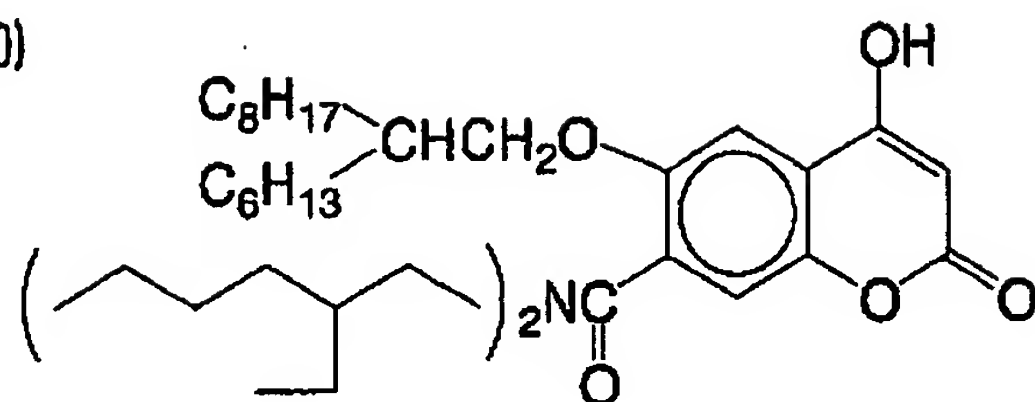


(B-19)

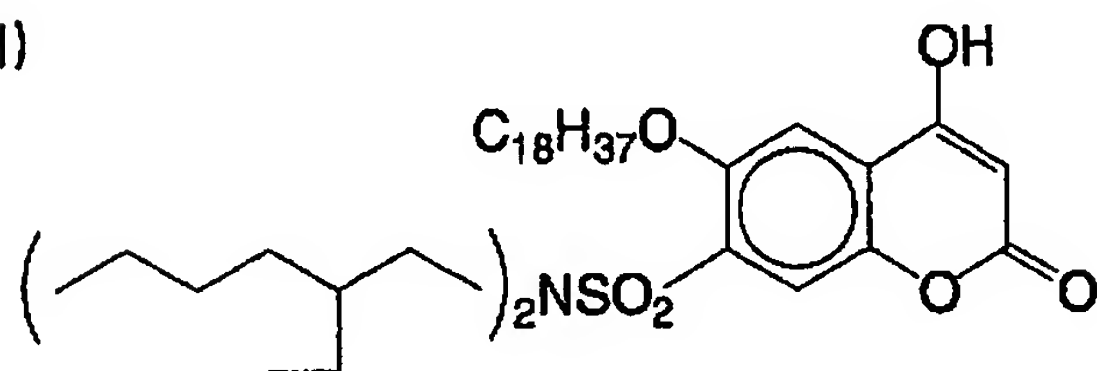


[0066]

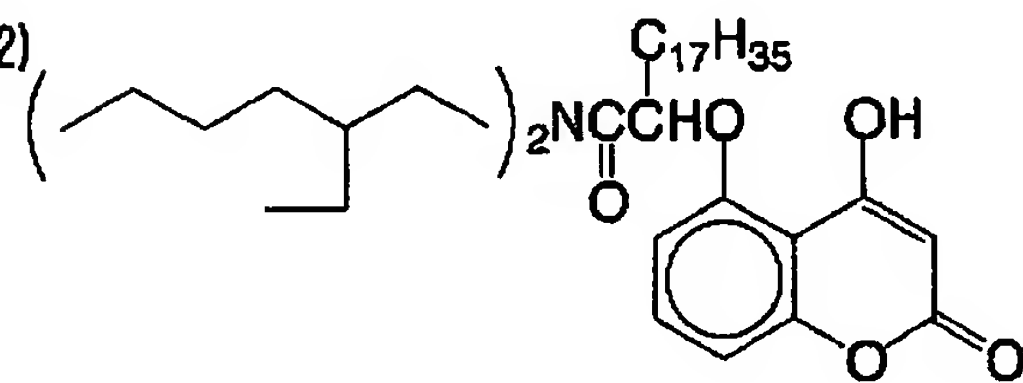
(B-20)



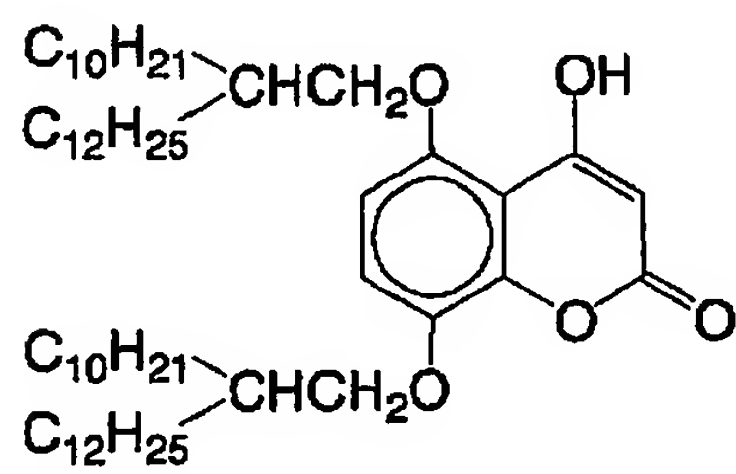
(B-21)



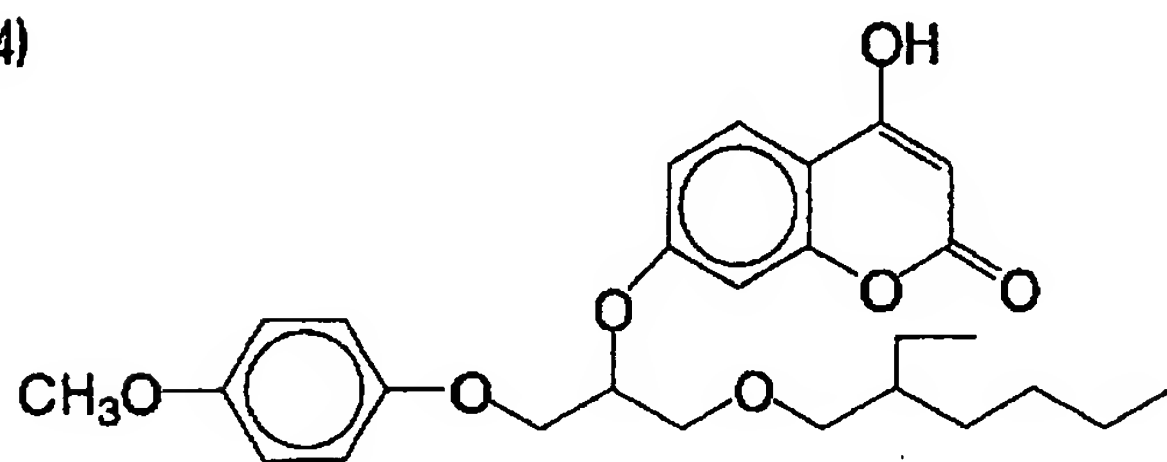
(B-22)



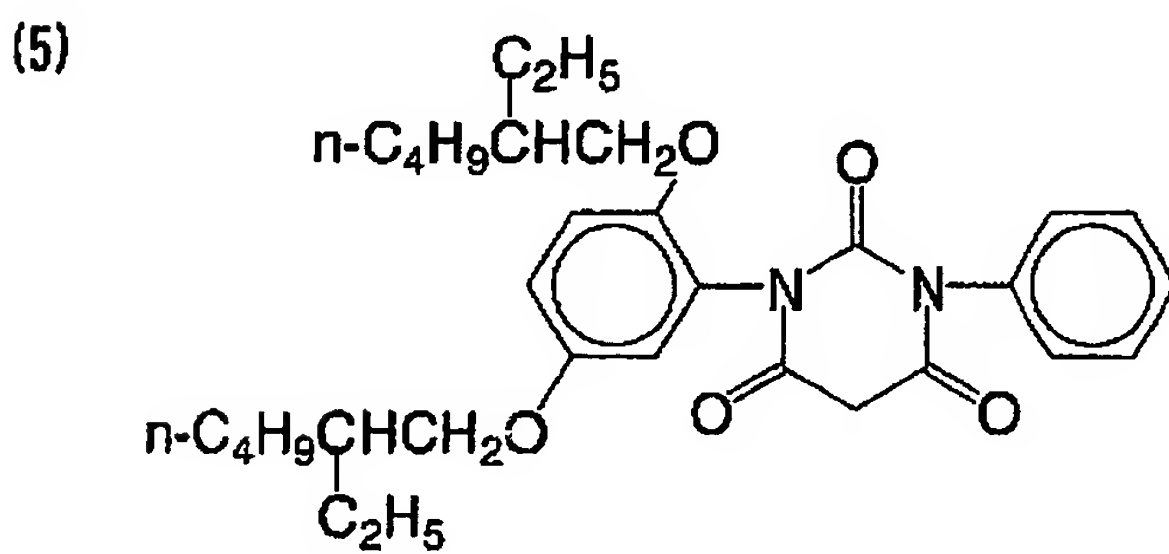
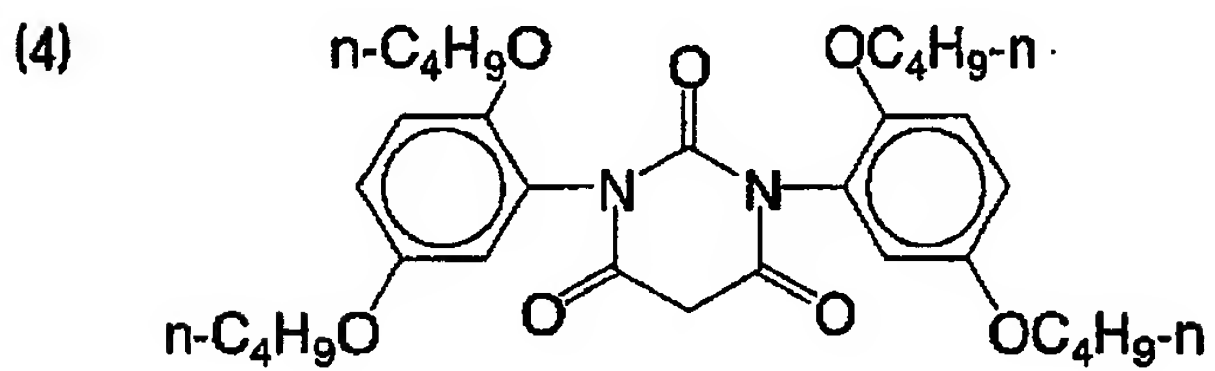
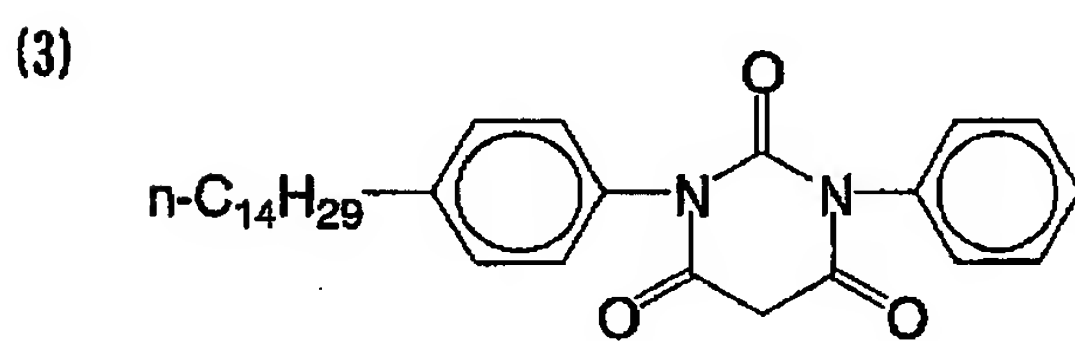
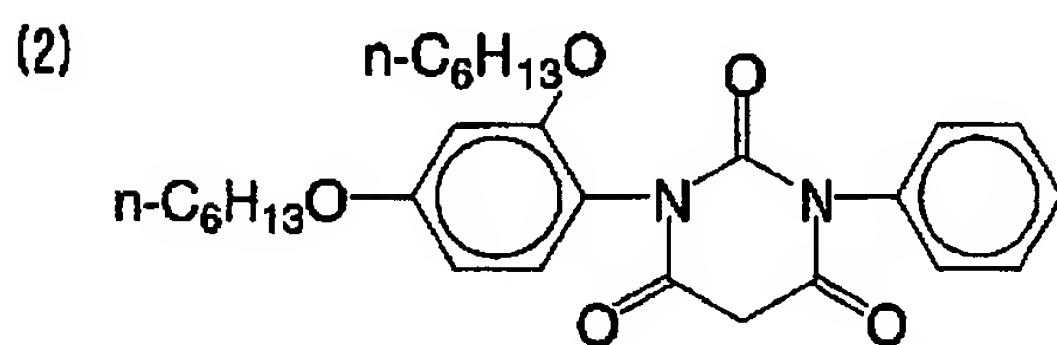
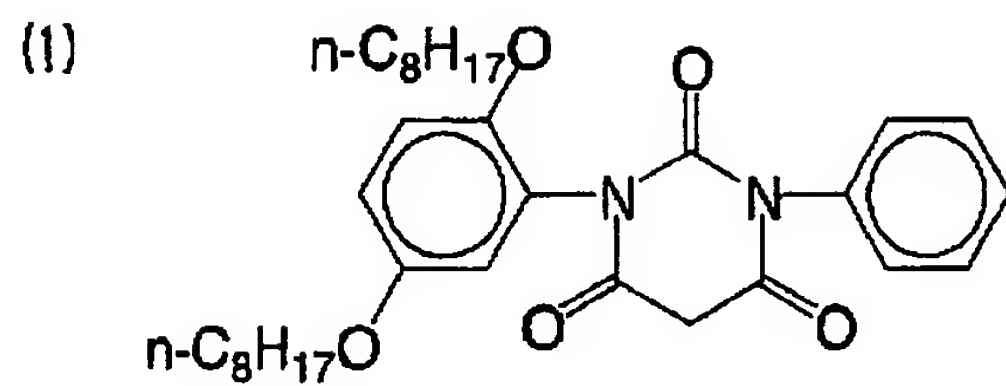
(B-23)



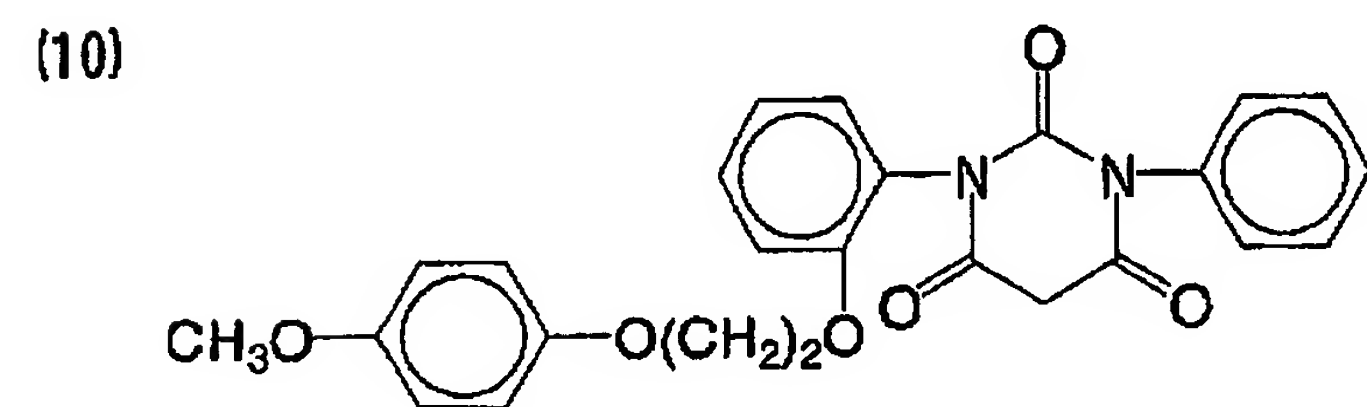
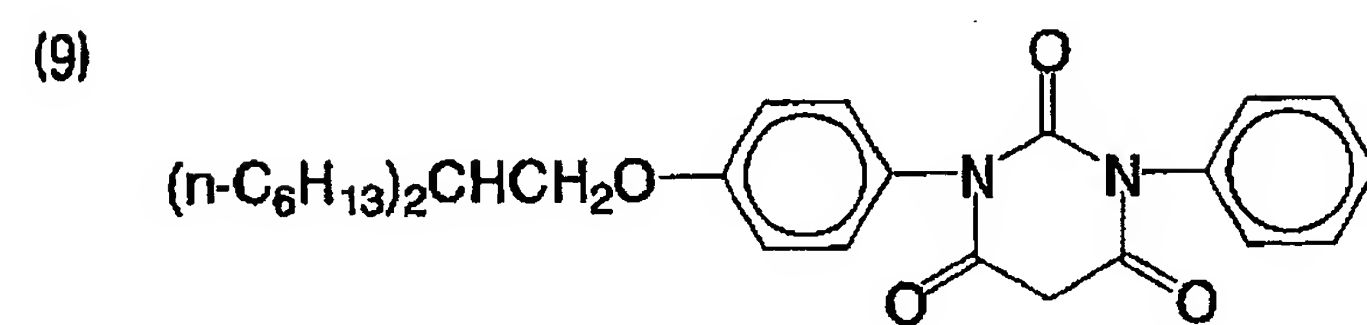
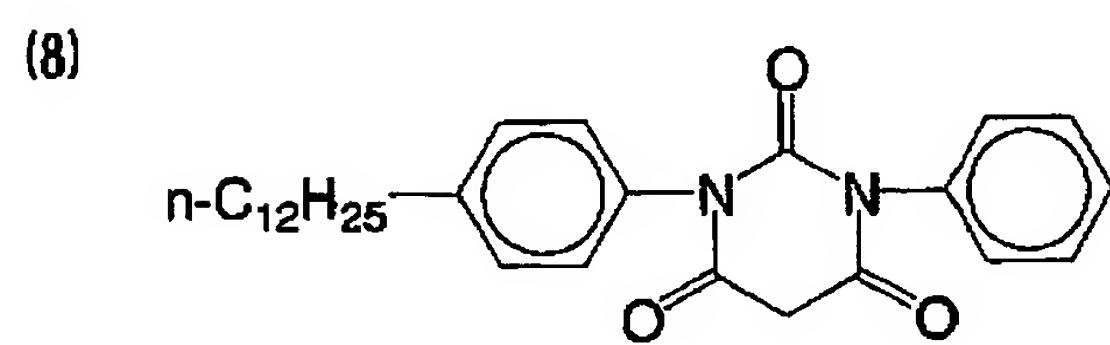
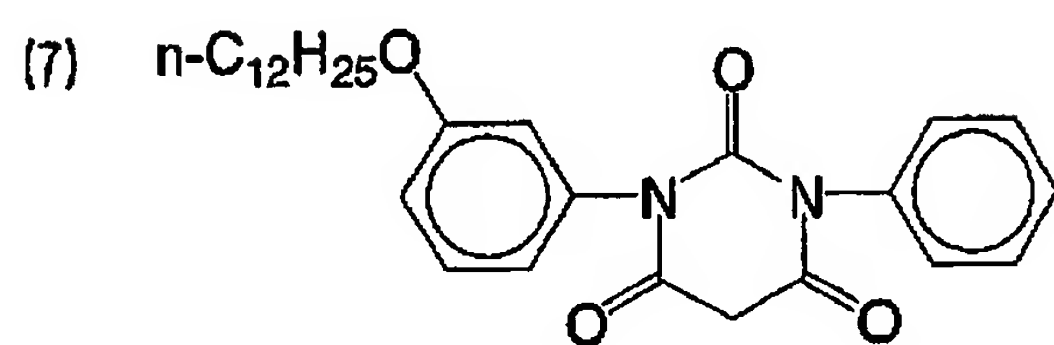
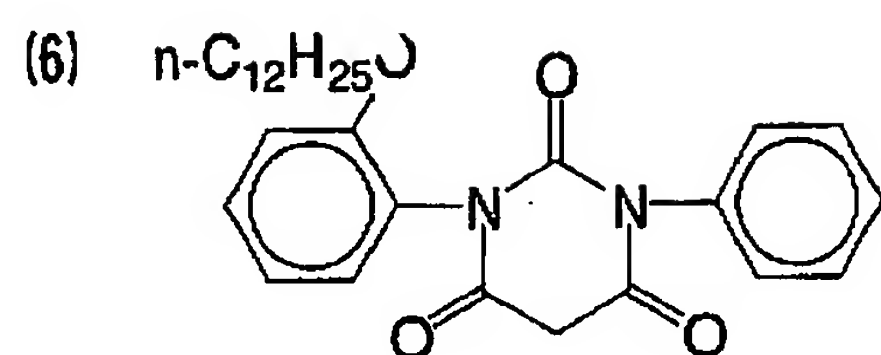
(B-24)



[0067]

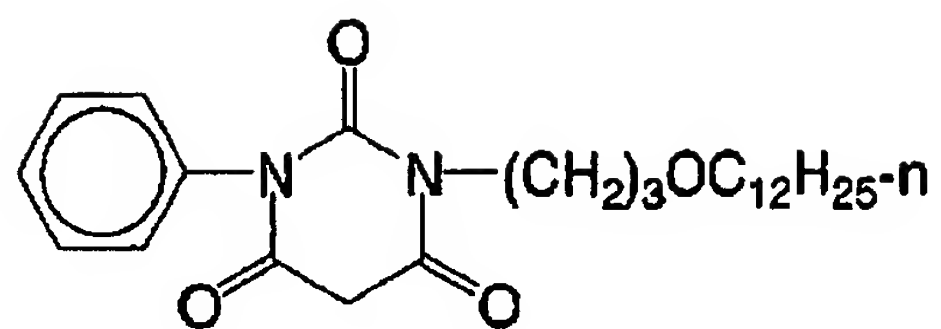


[0068]

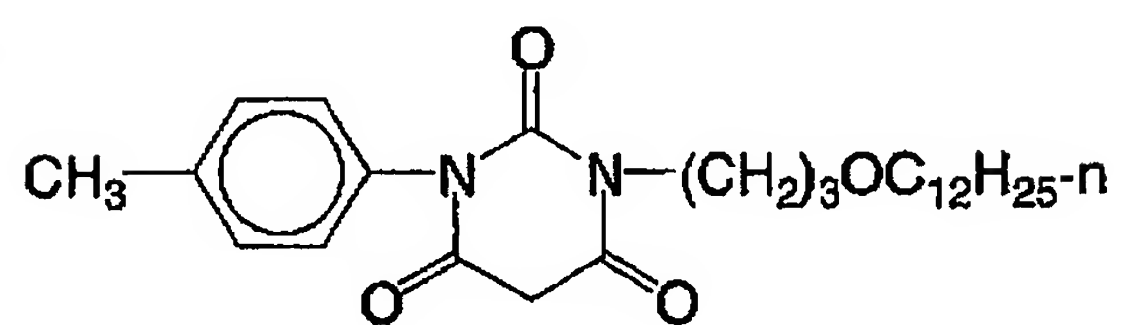


[0069]

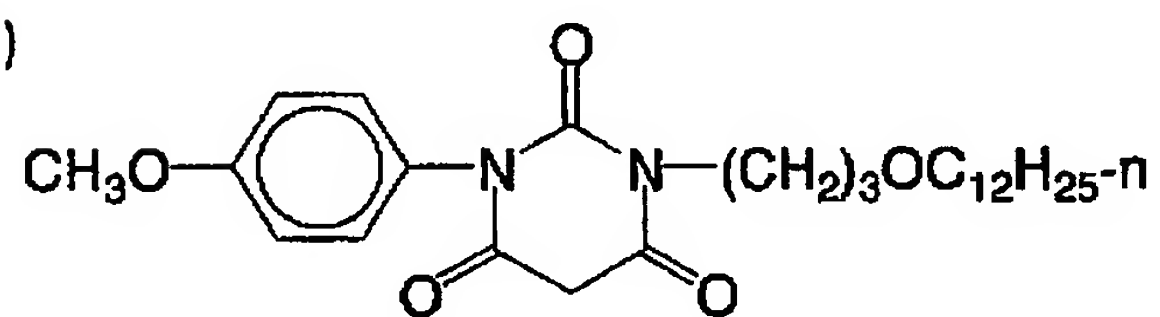
(11)



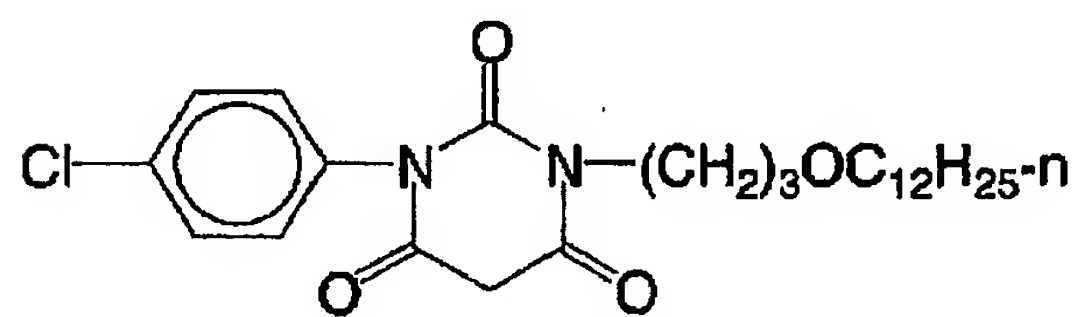
(12)



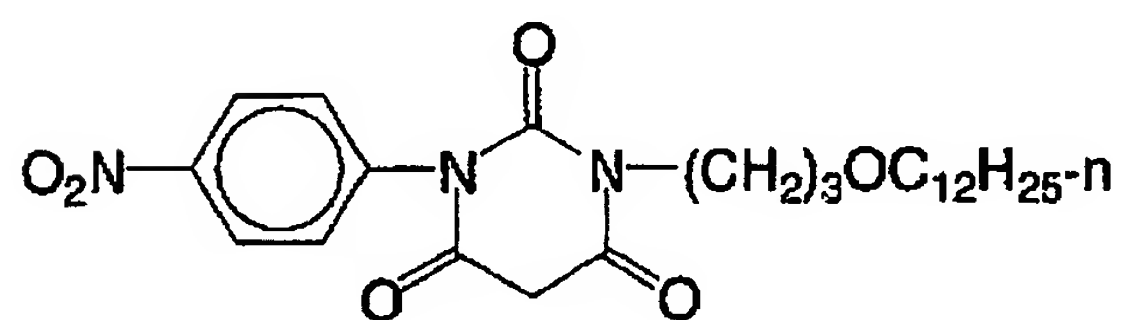
(13)



(14)

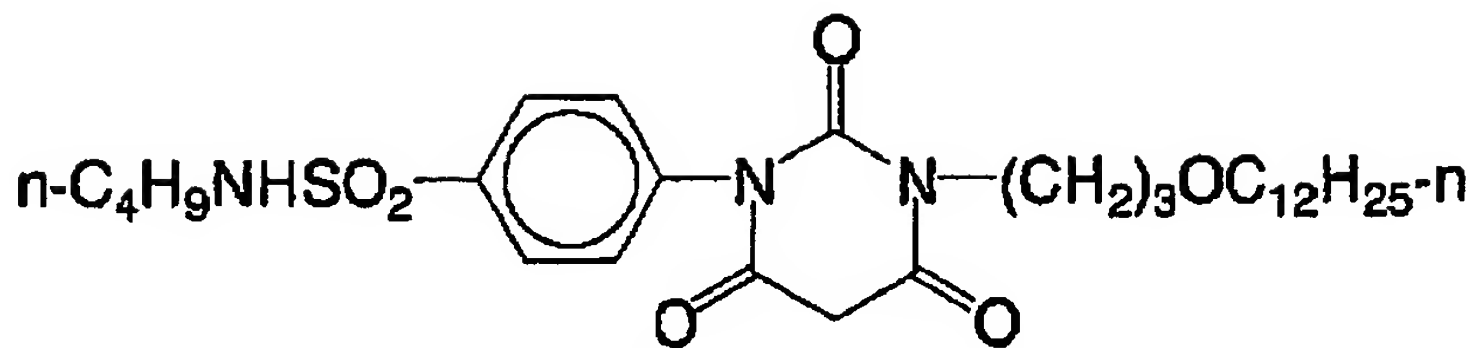


(15)

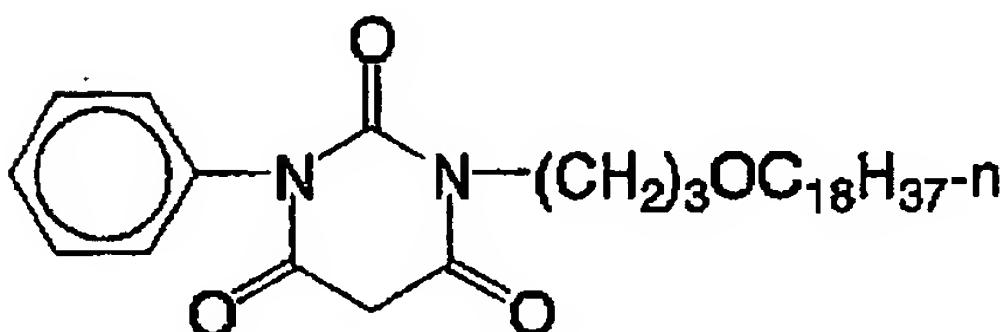


[0070]

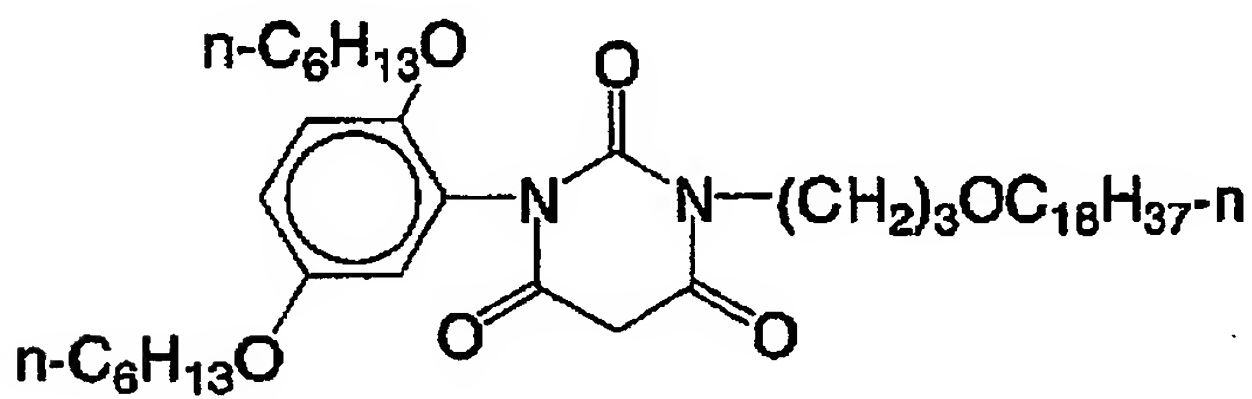
(16)



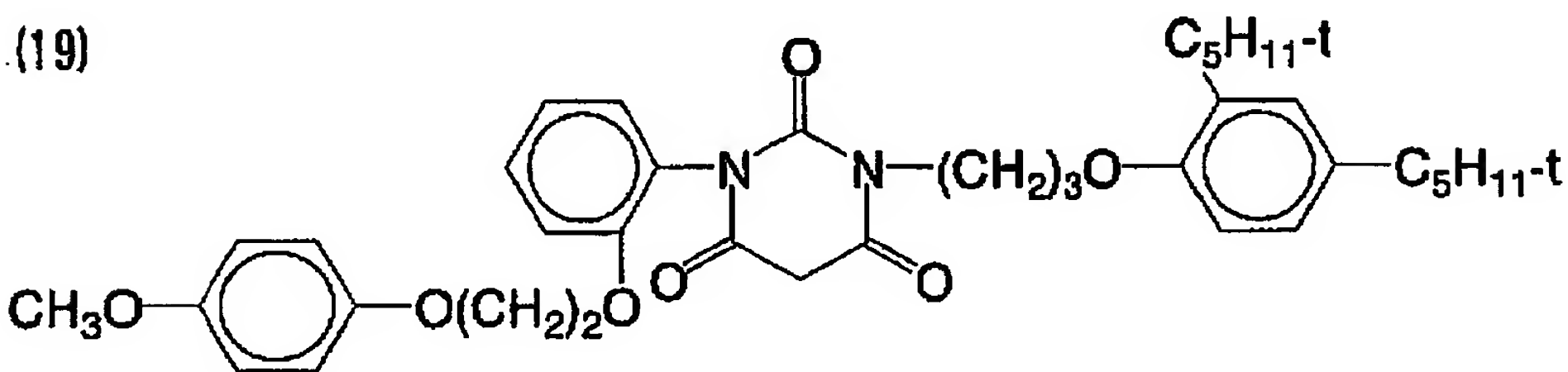
(17)



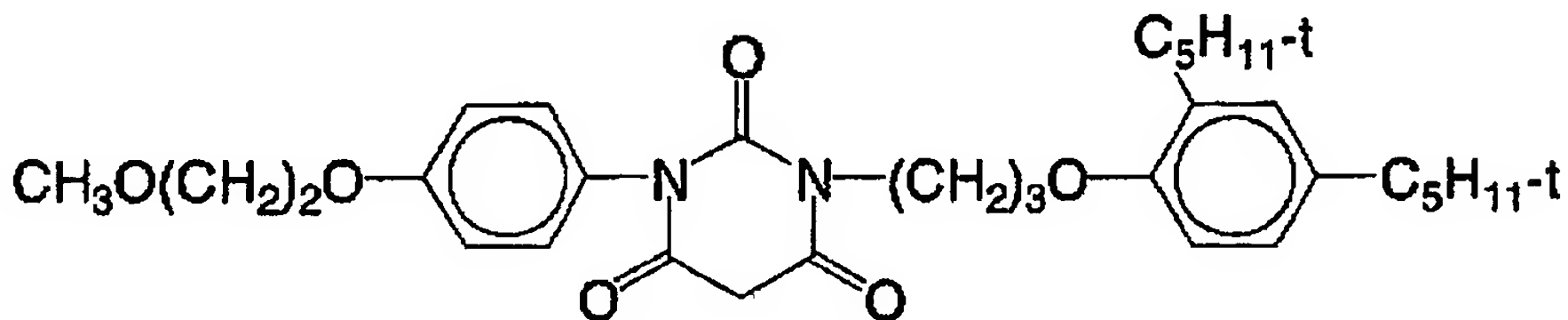
(18)



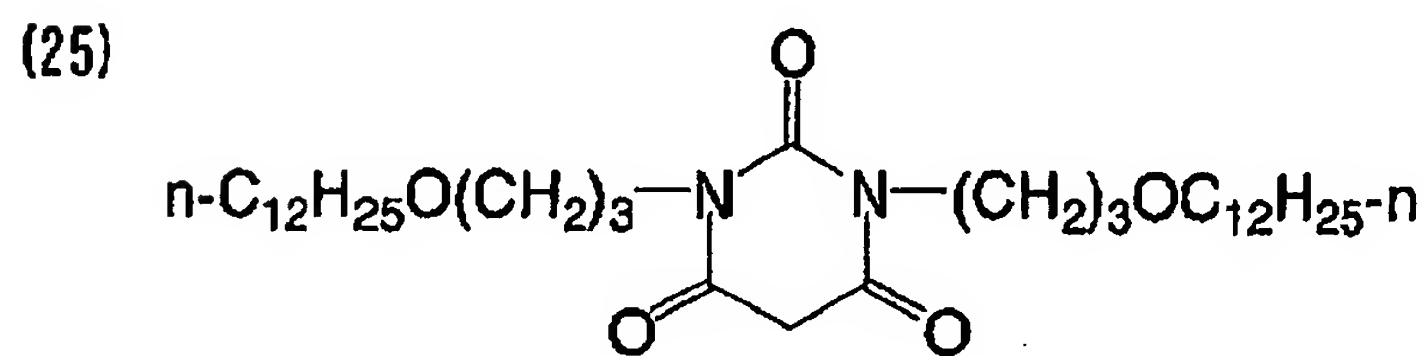
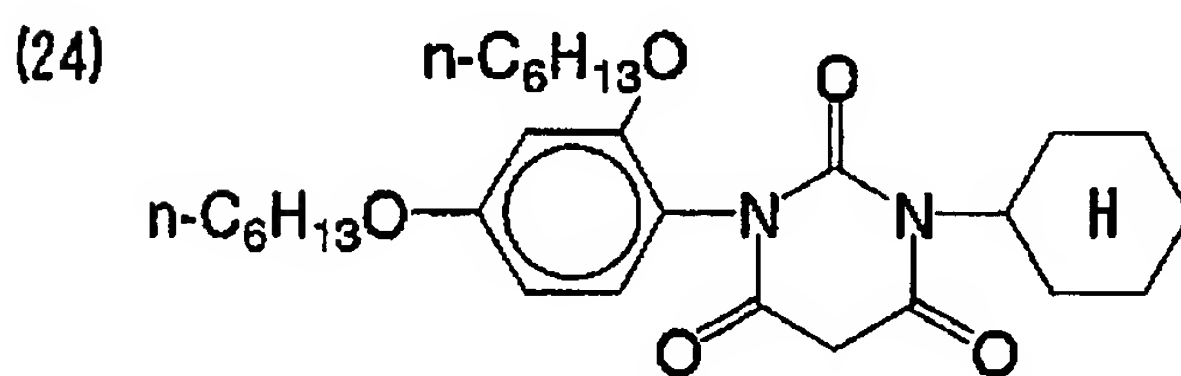
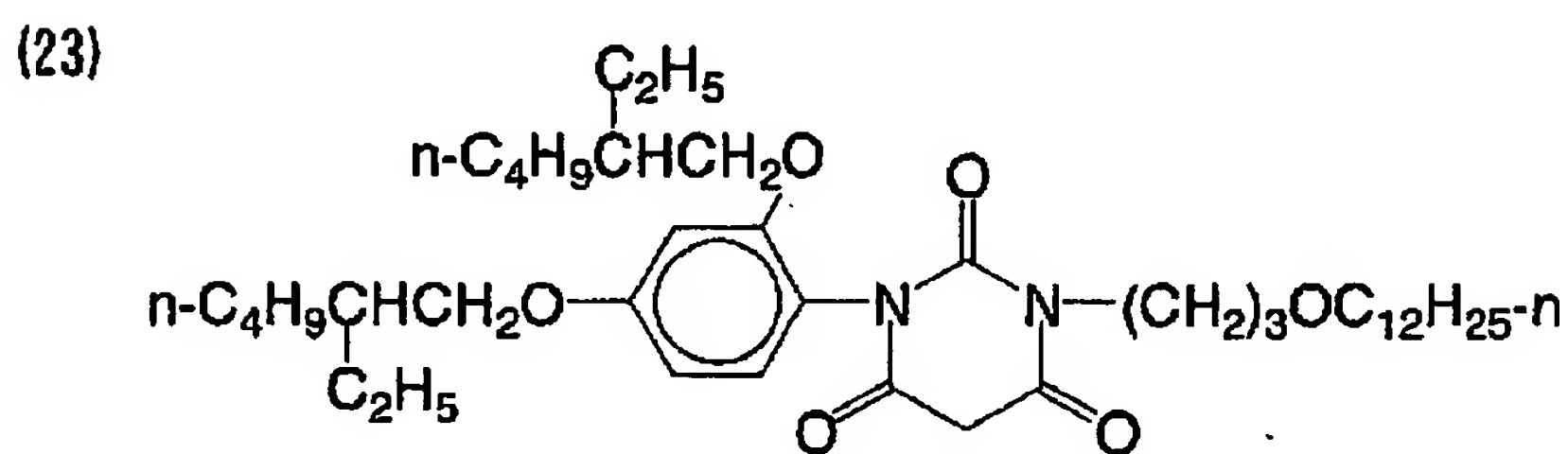
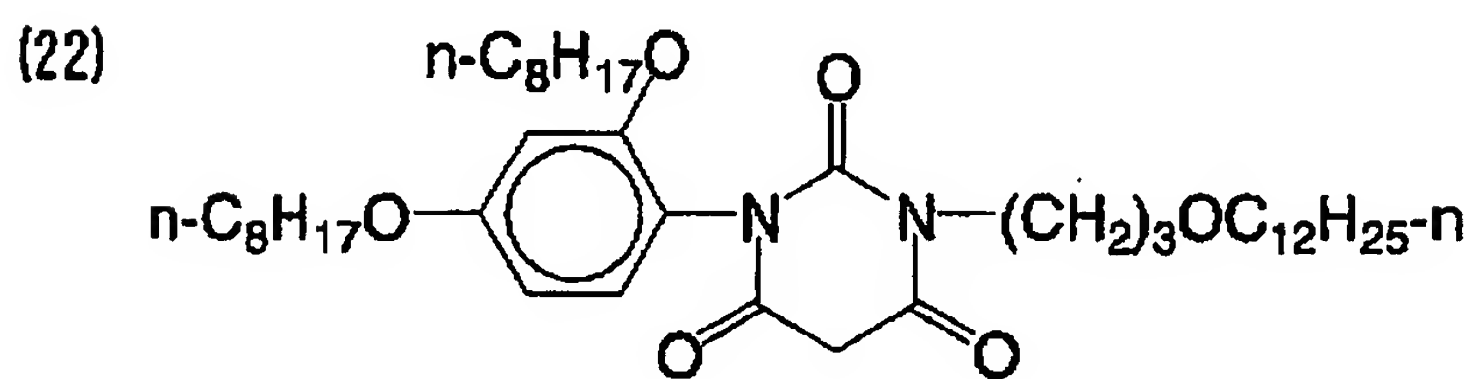
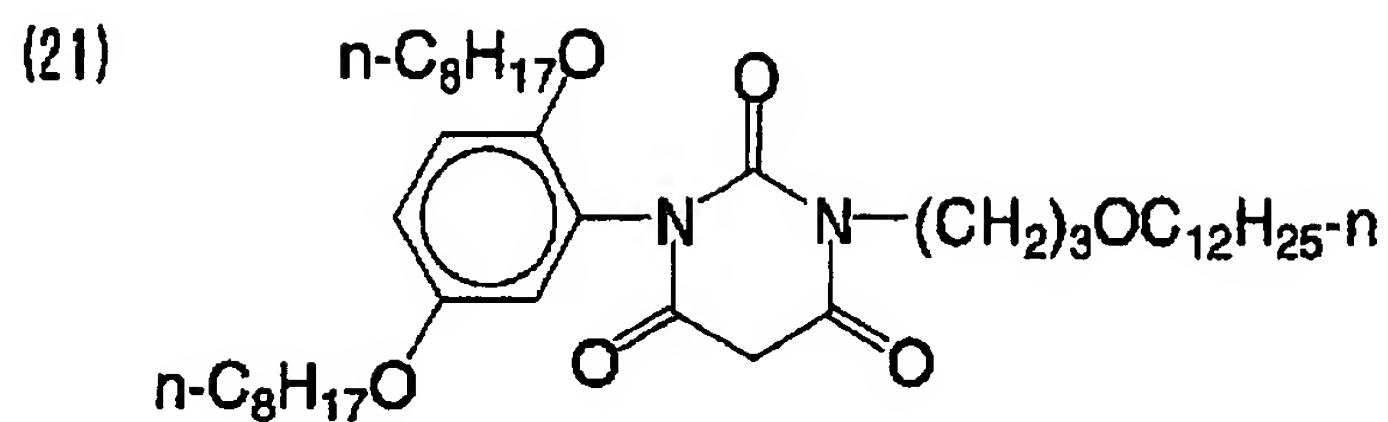
(19)



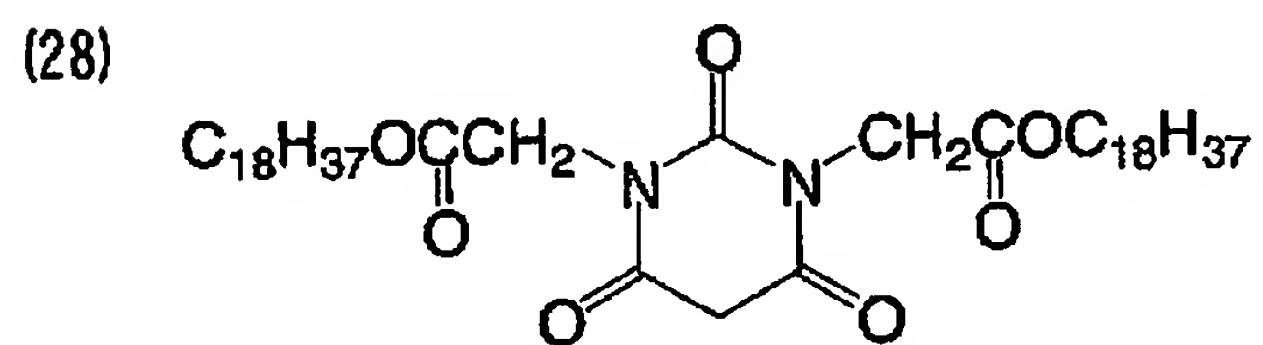
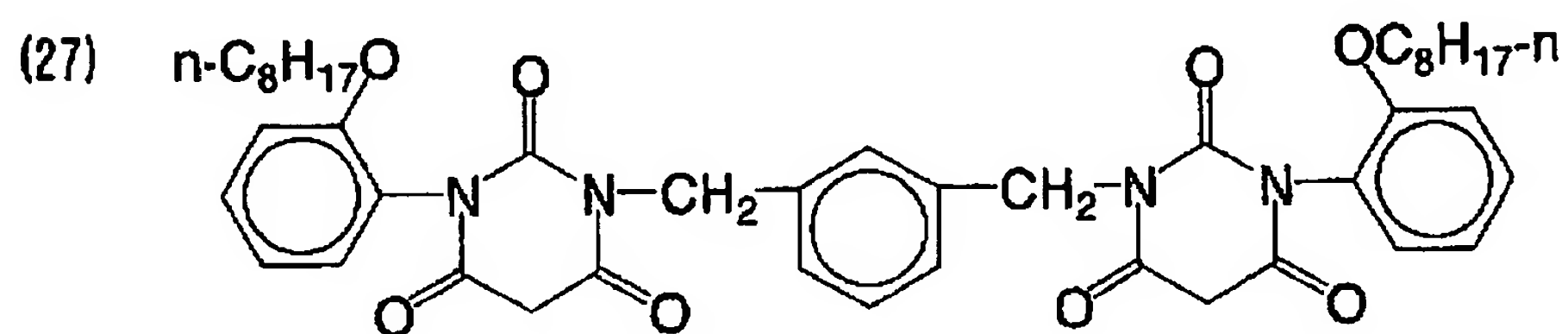
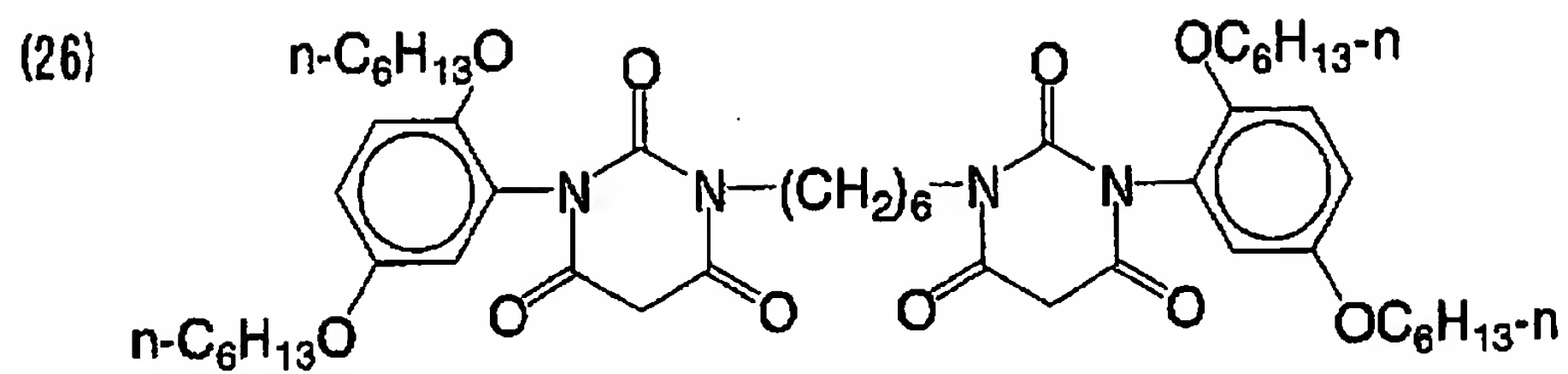
(20)



[0071]

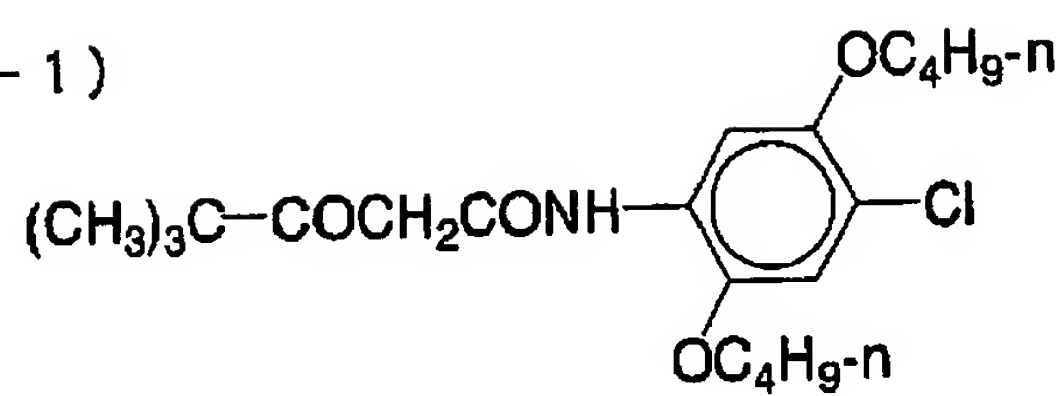


[0072]

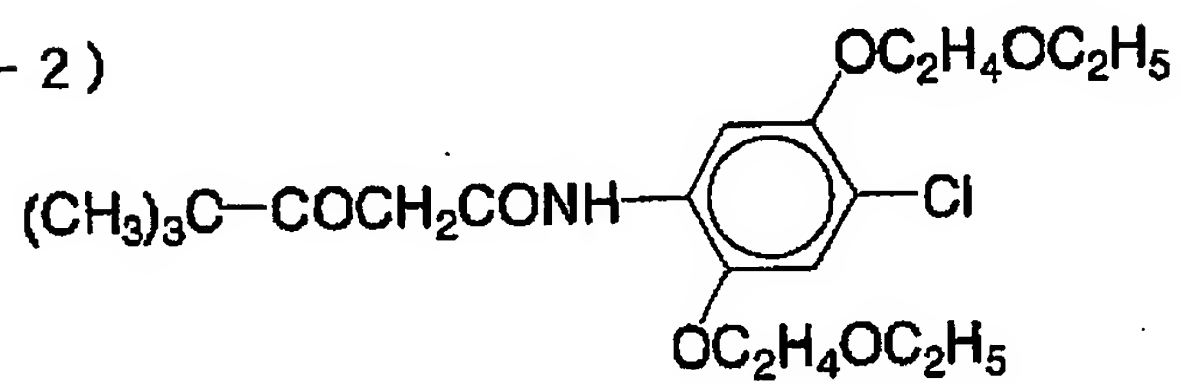


[0073]

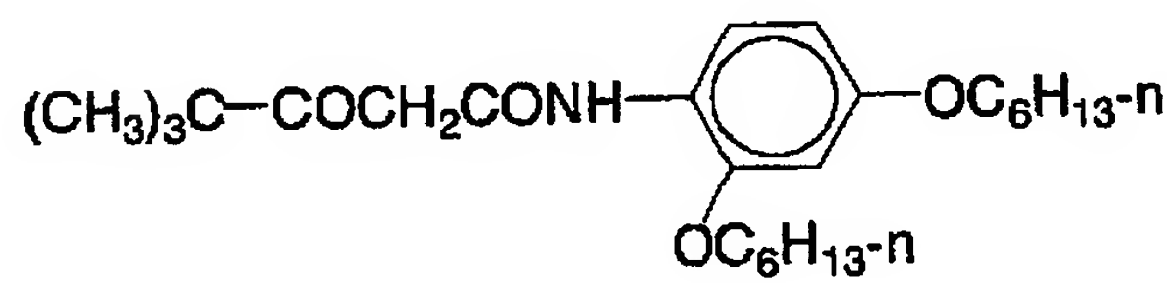
(II - 1)



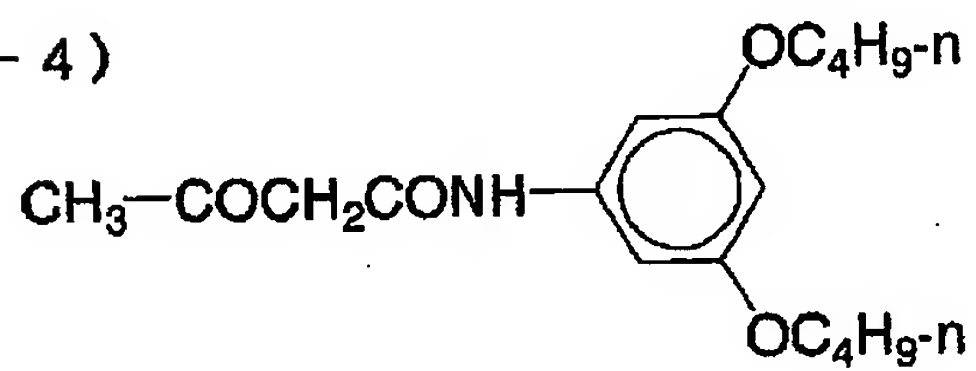
(II - 2)



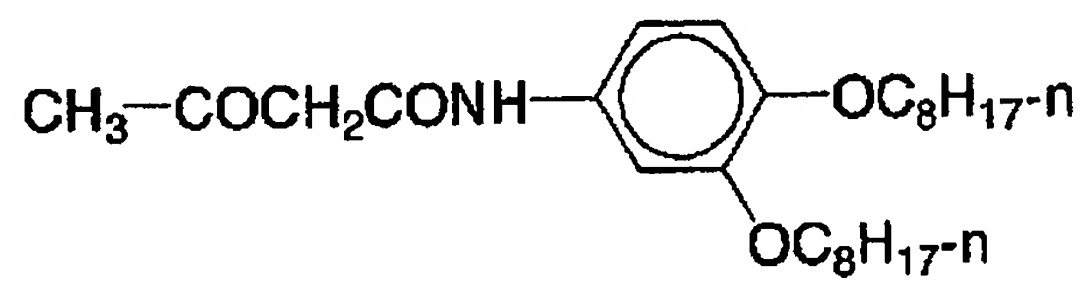
(II - 3)



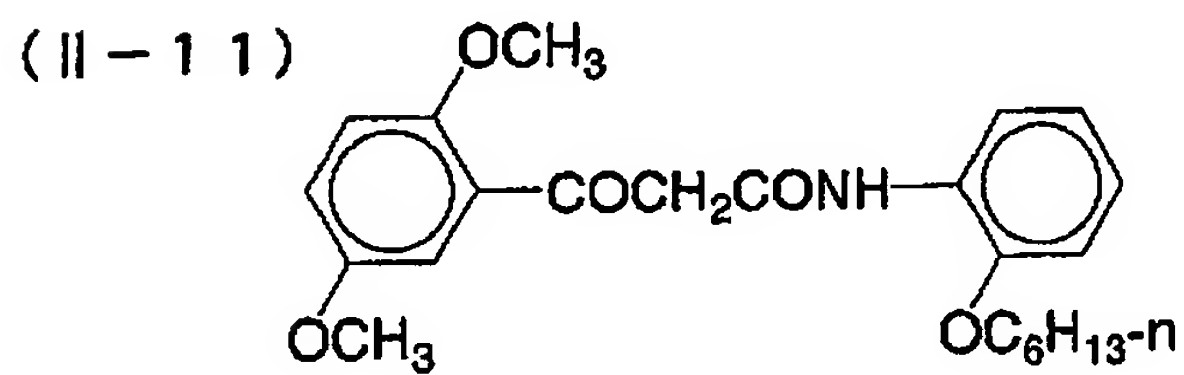
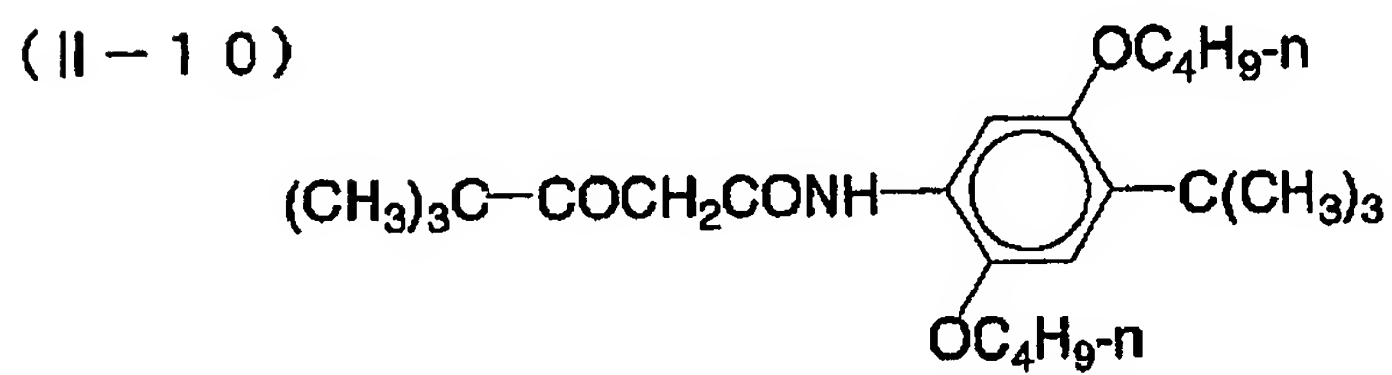
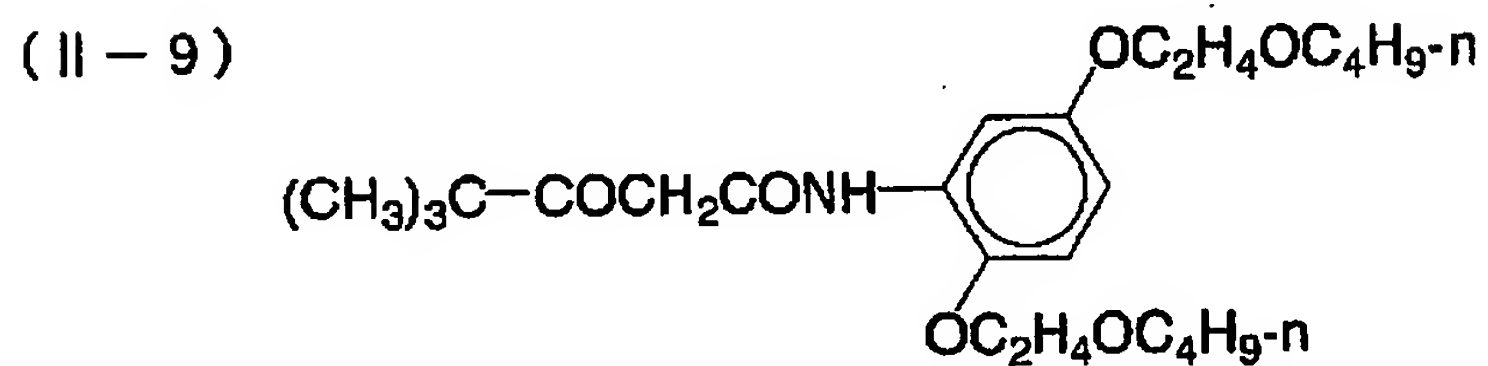
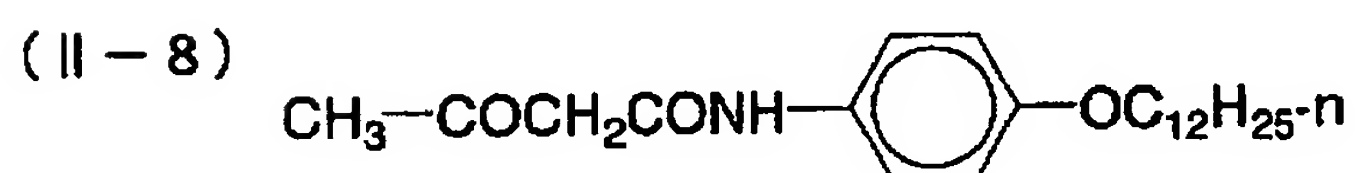
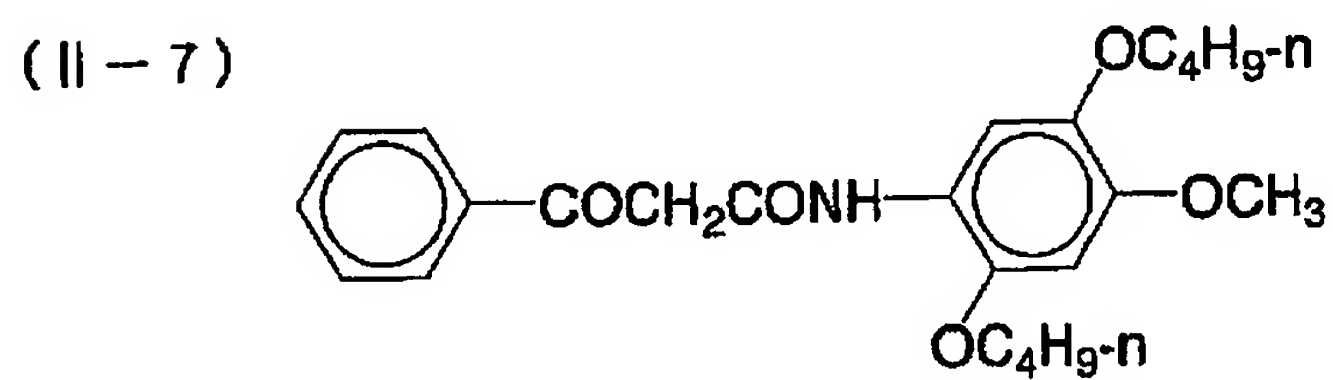
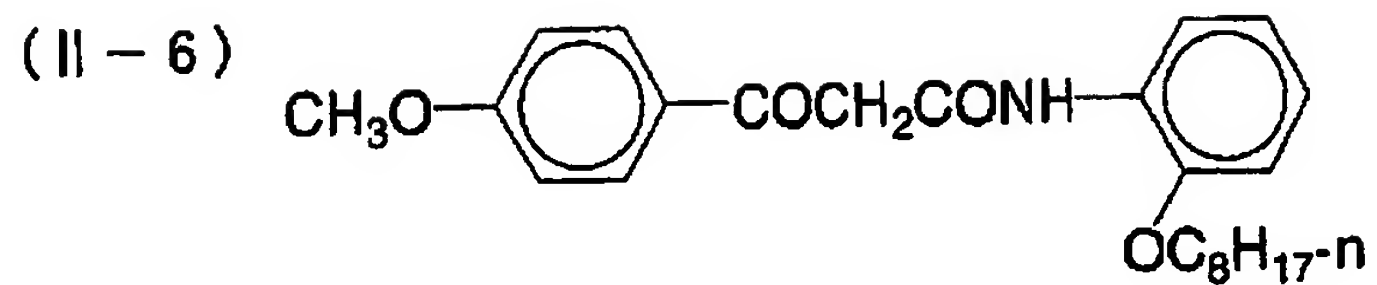
(II - 4)



(II - 5)

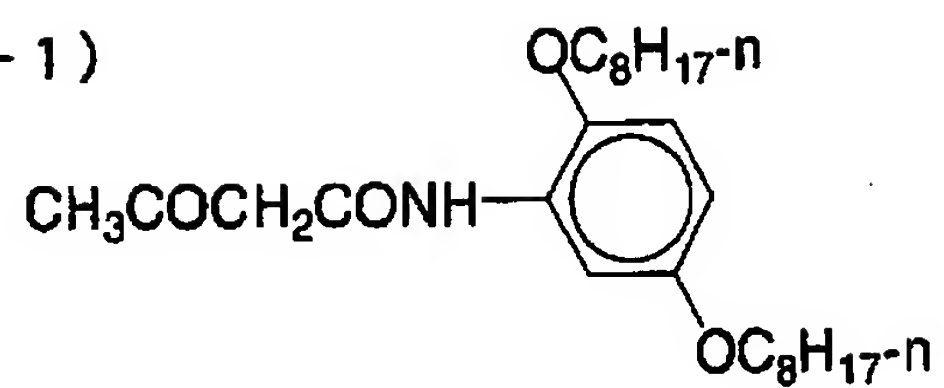


[0074]

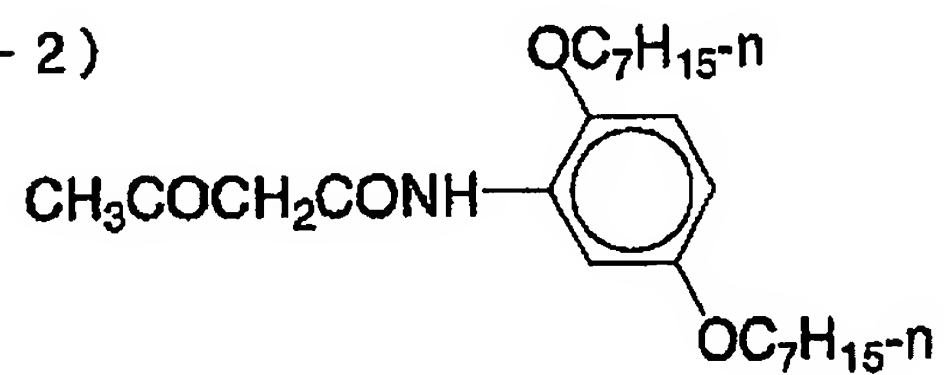


[0075]

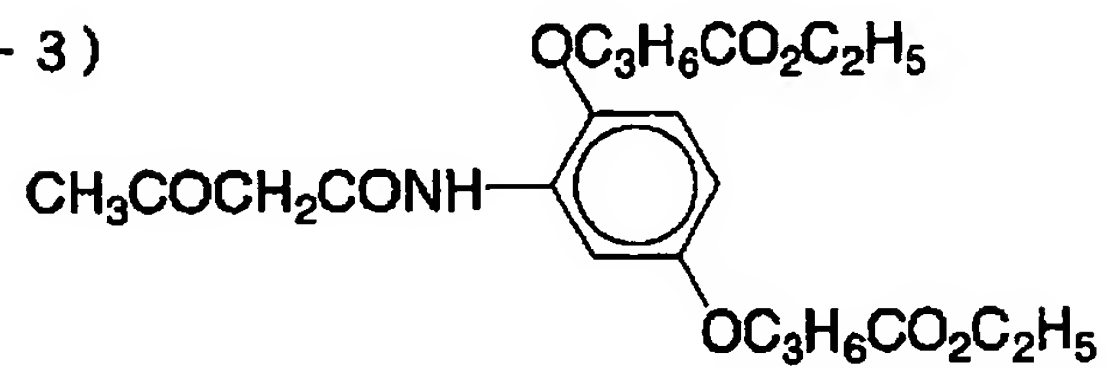
(VI-1)



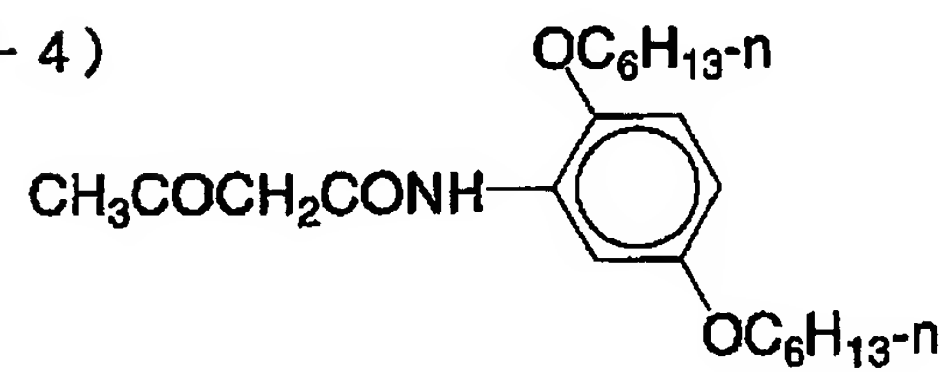
(VI-2)



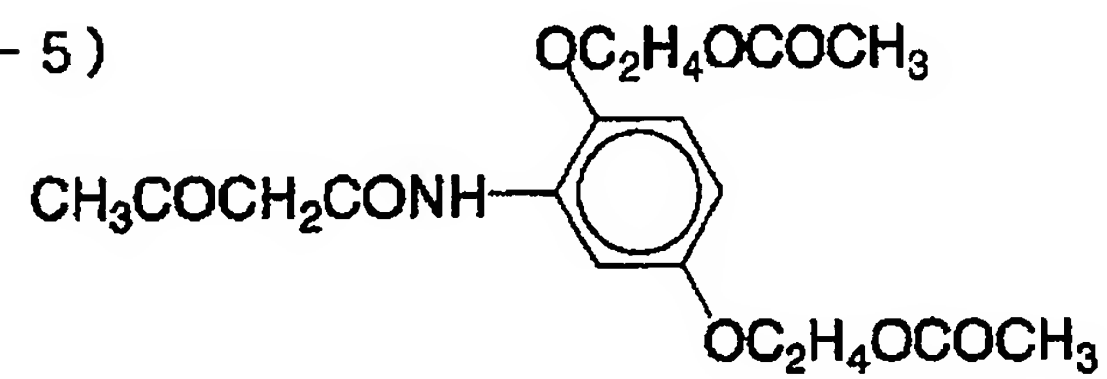
(VI-3)



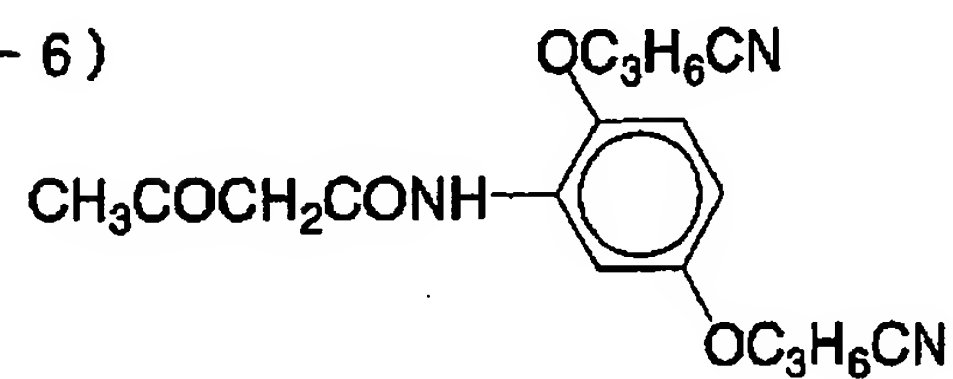
(VI-4)



(VI-5)



(VI-6)



[0076]

(Specific example of base)

The base may be used singly or in combination of two or more types. Examples of the base include a nitrogen-containing compound such as a tertiary amide, a piperidine, a piperadine, an amidine, a formamidine, a pyridine, a guanidine, and a morpholine.

[0077]

Particularly preferred examples of the bases include:

a piperadine such as N,N'-bis(3-phenoxy-2-hydroxypropyl)piperadine,
N,N'-bis(3-(p-methylphenoxy)-2-hydroxypropyl)piperadine,
N,N'-bis(3-(p-methoxyphenoxy)-2-hydroxypropyl)piperadine,
N,N'-bis(3-phenylthio-2-hydroxypropyl)piperadine,
N,N'-bis(3-(β -naphthoxy)-2-hydroxypropyl)piperadine,
N-3-(β -naphthoxy)-2-hydroxypropyl-N'-methylpiperadine, or
1,4-bis((3-N-methylpiperadino)-2-hydroxy)propyloxy)benzene,
a morpholine such as
N-(3-(β -naphthoxy)-2-hydroxy)propylmorpholine,
1,4-bis((3-morpholino-2-hydroxy)propyloxy)benzene or 1,3-bis((3-morpholino-2-hydroxy)propyloxy)benzene;

a piperidine such as N-(3-phenoxy-2-hydroxypropyl)piperidine or N-dodecylpiperidine; or a guanidine such as triphenylguanidine, tricyclohexylguanidine, or dicyclohexylphenylguanidine.

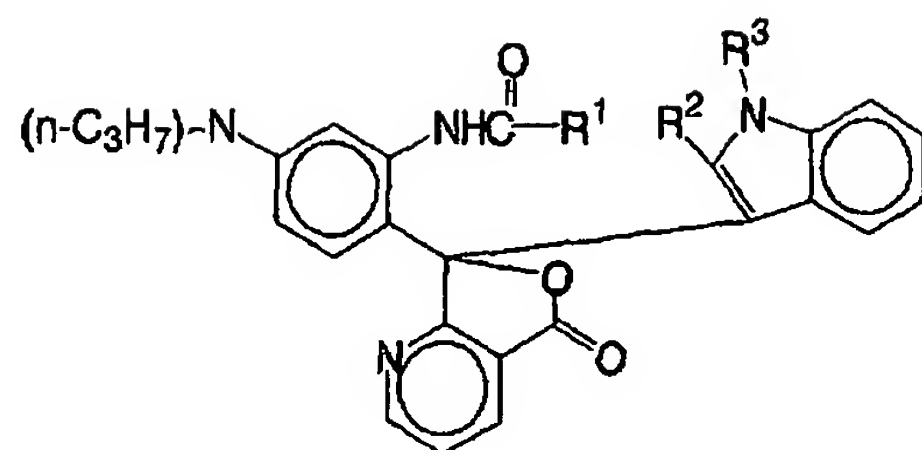
[0078]

The electron donating colorless dye and the electron accepting compound mentioned in the foregoing are described in detail, for example, in JP-A Nos. 6-328860, 7-290826, 7-314904, 8-324116, 3-37727, 9-31345, 9-111136, 9-118073, and 11-157221. Specific examples are shown below, however, the invention is not limited to such examples.

[0079]

-Specific examples of electron donating colorless dye-

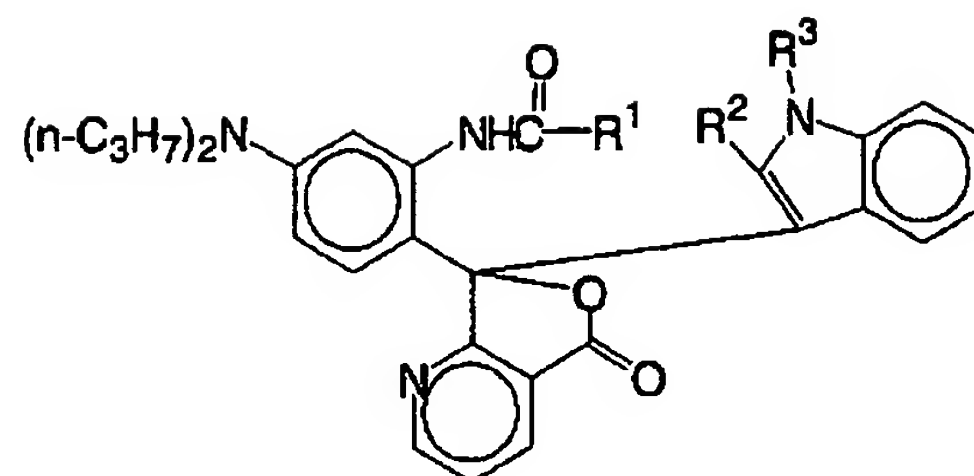
Table 1



	R ¹	R ²	R ³
i-1	-CH ₃	-CH ₃	-C ₂ H ₅
i-2	-C ₂ H ₅	-CH ₃	-C ₂ H ₅
i-3	-CH(CH ₃) ₂	-CH ₃	-C ₂ H ₅
i-4	-C(CH ₃) ₃	-CH ₃	-C ₂ H ₅
i-5		-CH ₃	-C ₂ H ₅
i-6		-CH ₃	-C ₂ H ₅
i-7	-CH ₂ OCH ₃	-CH ₃	-C ₂ H ₅
i-8	-CH ₂ Cl	-CH ₃	-C ₂ H ₅
i-9	-CCl ₃	-CH ₃	-C ₂ H ₅
i-10	-CF ₃	-CH ₃	-C ₂ H ₅
i-11		-CH ₃	-C ₂ H ₅
i-12		-CH ₃	-C ₂ H ₅
i-13	-C ₃ H ₇ (n)	-CH ₃	-C ₂ H ₅
i-14	-CH ₃	-CH ₃	-C ₄ H ₉ (n)
i-15	-CH ₃	-CH ₃	-C ₈ H ₁₇ (n)
i-16	-CH(CH ₃) ₂	-CH ₃	-C ₄ H ₉ (n)
i-17		-CH ₃	-C ₆ H ₁₁ (n)
i-18	-CH ₂ OCH ₃	-CH ₃	-C ₈ H ₁₇ (n)

[0080]

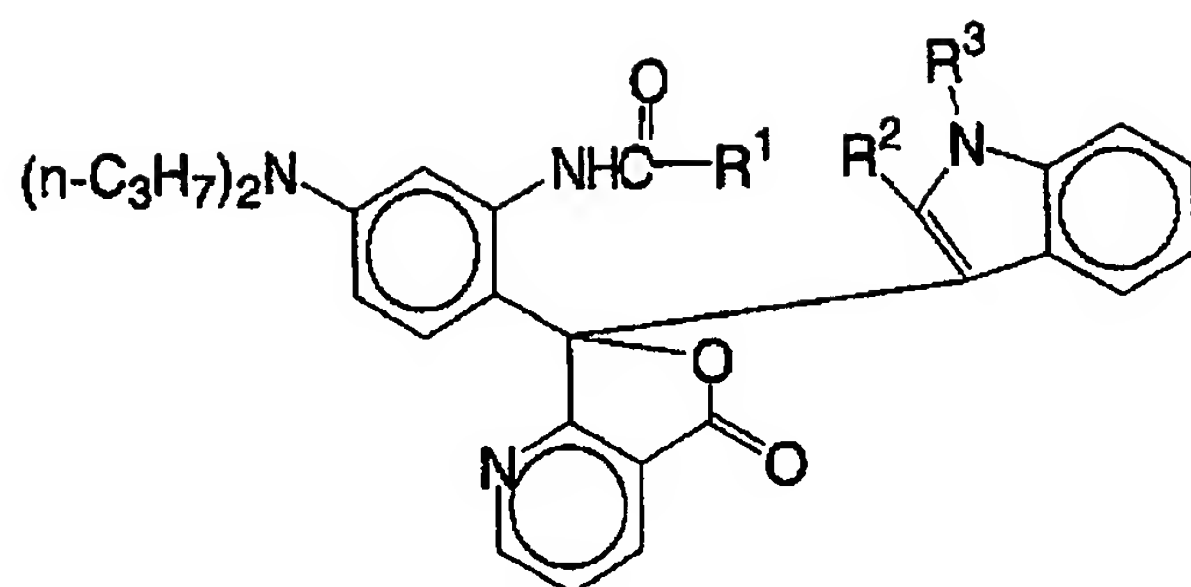
Table 2

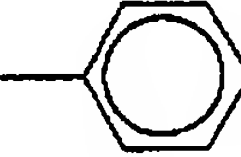
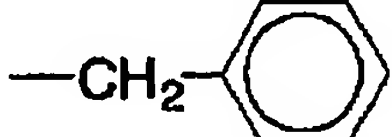
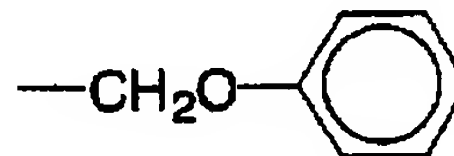
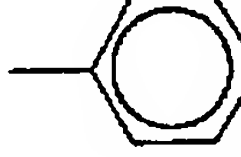
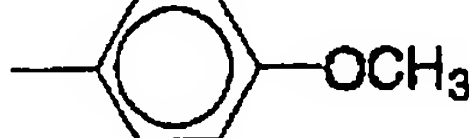


	R ¹	R ²	R ³
i-19	-CH ₃	-CH ₃	
i-20		-CH ₃	-C ₆ H ₁₃ (n)
i-21	-CH ₃		-C ₂ H ₅
i-22	-CH ₃		-C ₈ H ₁₇ (n)
ia-1	-C ₈ H ₁₁ (n)	-CH ₃	-C ₂ H ₅
ia-2	-C ₇ H ₁₅ (n)	-CH ₃	-C ₂ H ₅
ia-3	-C ₁₇ H ₃₅ (n)	-CH ₃	-C ₂ H ₅
ia-4		-CH ₃	-C ₂ H ₅
ia-5		-CH ₃	-C ₂ H ₅
ia-6		-CH ₃	-C ₂ H ₅
ia-7	-CH ₃	-CH ₃	-C ₅ H ₁₁ (n)
ia-8	-CH ₃	-CH ₃	-CH(CH ₃) ₂
ia-9	-C ₃ H ₇ (n)	-CH ₃	-C ₈ H ₁₇ (n)
ia-10	-C ₄ H ₉ (n)	-CH ₃	-C ₈ H ₁₇ (n)

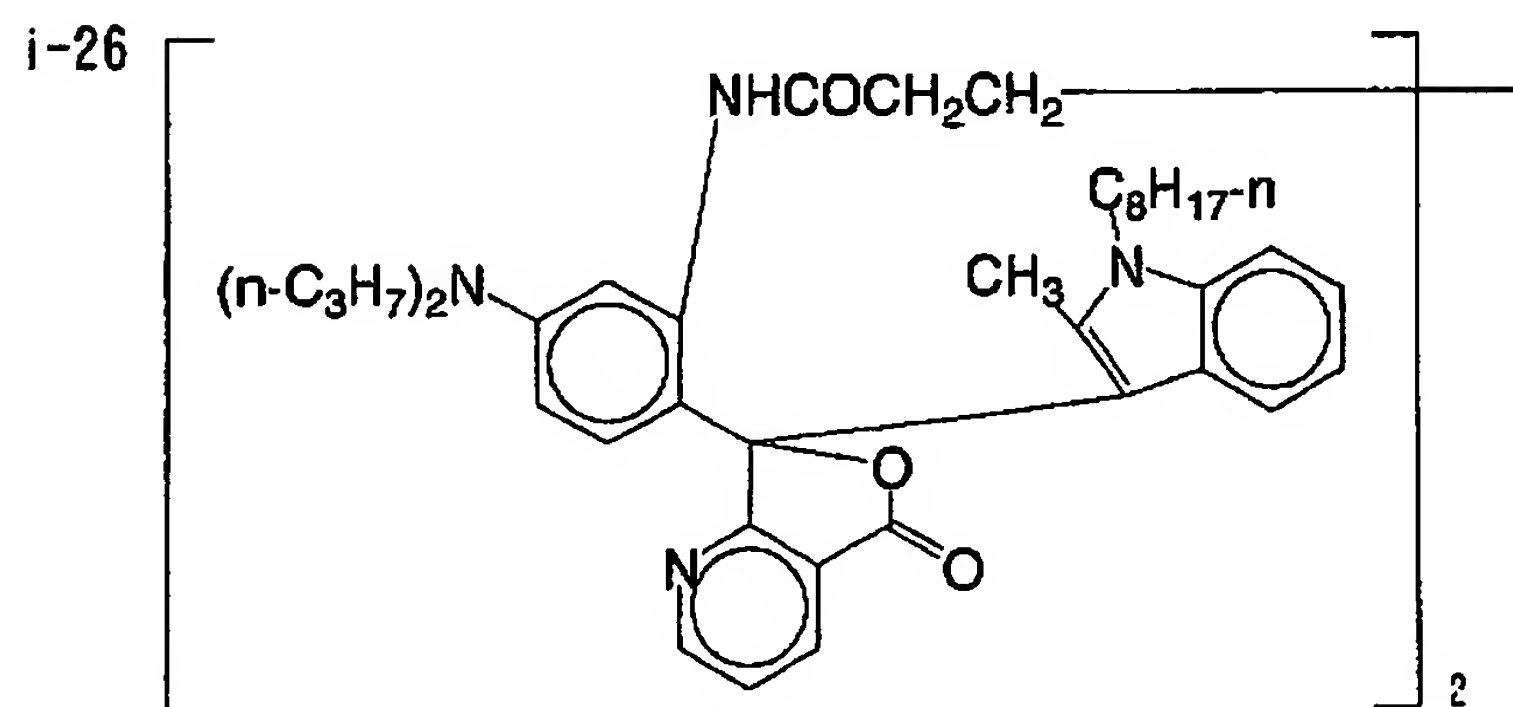
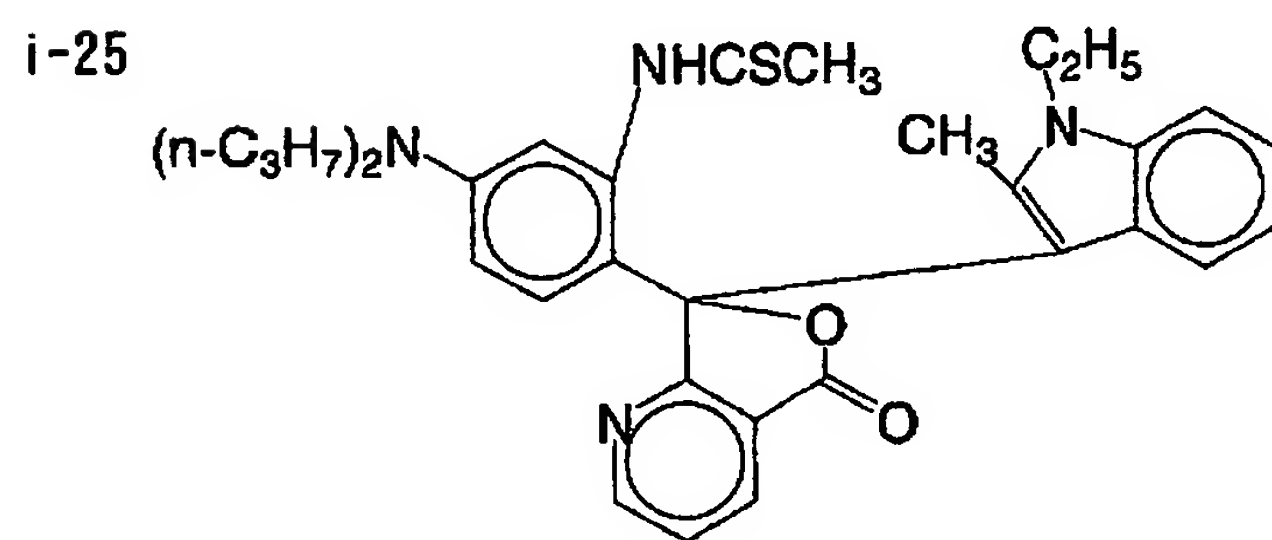
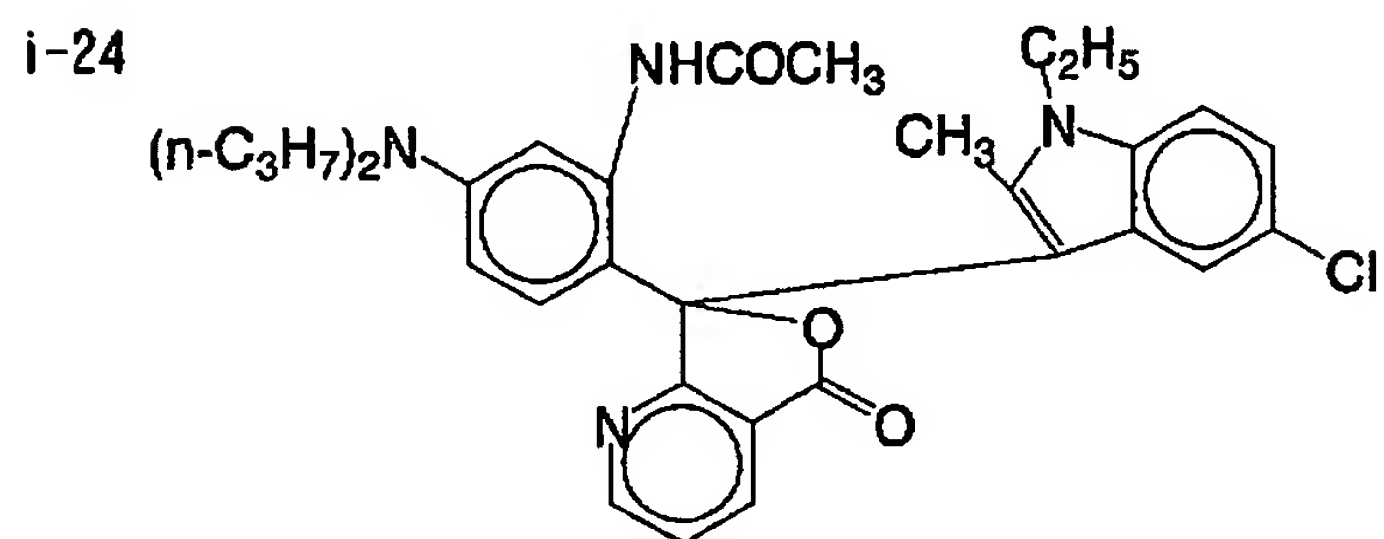
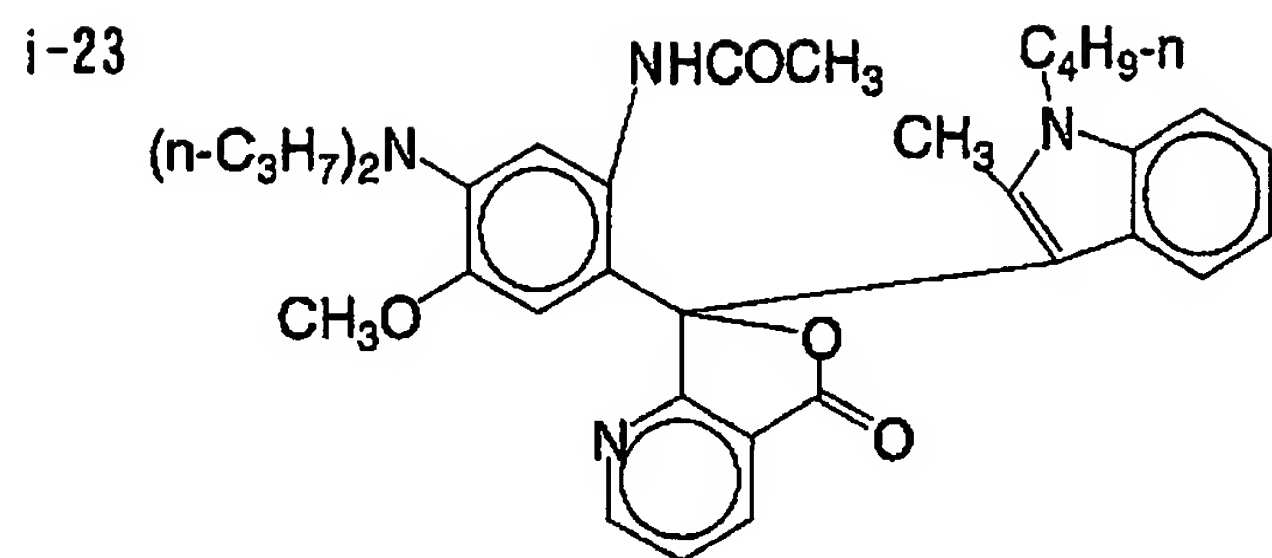
[0081]

Table 3



	R ¹	R ²	R ³
ia-11	-CH(CH ₃) ₂	-CH ₃	-C ₈ H ₁₇ (n)
ia-12	-C ₃ H ₇ (t)	-CH ₃	-C ₈ H ₁₇ (n)
ia-13	-C ₄ H ₉ (t)	-CH ₃	-C ₈ H ₁₇ (n)
ia-14		-CH ₃	-C ₈ H ₁₇ (n)
ia-15		-CH ₃	-C ₈ H ₁₇ (n)
ia-16		-CH ₃	-C ₈ H ₁₇ (n)
ia-17	-C ₃ H ₇ (n)	-CH ₃	
ia-18	-CH ₃	-CH ₃	

[0082]



[0083]

(Specific examples of electron accepting compounds)

The electron accepting compound can be a phenol derivative, a salicylic acid derivative or a hydroxybenzoic acid ester. For the electron accepting compound, particularly preferred are a bisphenol and a hydroxybenzoic acid ester. Specific examples of particularly preferred electron accepting compounds include:

2,2-bis(p-hydroxyphenyl)propane (namely bisphenol-A),
4,4'-(p-phenylenediisopropylidene)diphenyl (namely bisphenol-P), 2,2-bis(p-hydroxyphenyl)pentane,
2,2-bis(p-hydroxyphenyl)ethane,
2,2-bis(p-hydroxyphenyl)butane,
2,2-bis(4'-hydroxy-3',5'-dichlorophenyl)propane,
1,1-(p-hydroxyphenyl)cyclohexane,
1,1-(p-hydroxyphenyl)propane,
1,1-(p-hydroxyphenyl)pentane,
1,1-(p-hydroxyphenyl)-2-ethylhexane,
3,5-di(α -methylbenzyl)salicylic acid and a polyvalent metal salt thereof,
3,5-di(tert-butyl)salicylic acid and a polyvalent metal salt thereof,
3- α,α -dimethylbenzylsalicylic acid and a polyvalent metal salt thereof, butyl p-hydroxybenzoate, benzyl

p-hydroxybenzoate, 2-ethylhexyl p-hydroxybenzoate,
p-phenylphenol and p-cumylphenol.

[0084]

(Microcapsules)

In the invention, the mode of use of the diazonium compound, the coupler which forms a color by reaction under heating with the diazonium salt compound, the basic substance, the electron donating colorless dye, the electron accepting compound, the sensitizer, etc. is not particularly limited but can be suitably selected from (1) a method using solid dispersion; (2) a method using emulsification; (3) a method using polymer dispersion; (4) a method using latex dispersion; or (5) a method using microencapsulation. Among these methods, it is particularly preferable to use method (4) utilizing microencapsulation, in consideration of unprocessed stock storability. Particularly in a color forming system utilizing the reaction of a diazonium salt compound and a coupler, it is preferred to encapsulate the diazonium salt compound, and in a color forming reaction utilizing a reaction of an electron donating colorless dye and an electron accepting compound, it is preferred to encapsulate the electron donating colorless dye.

[0085]

For microencapsulation, there can be utilized a known microencapsulating method. A polymer substance forming a microcapsule wall must be impermeable at room temperature and become permeable when heated. The polymer substance preferably has a glass transition temperature within a range of 60 to 200°C. Specific examples of such substances include polyurethane, polyurea, polyamide, polyester, a urea-formaldehyde resin, a melamine resin, polystyrene, a styrene-methacrylate copolymer, a styrene-acrylate copolymer, and mixed systems thereof.

[0086]

For forming the microcapsules, an interfacial polymerization method or an internal polymerization method can be used. Details of these methods and specific examples of reactants are described, for example, in USP Nos. 3,726,804 and 3,796,669. For example, when employing polyurea or polyurethane as the microcapsule wall material, the microcapsule wall can be prepared by mixing a polyisocyanate and a second material capable of reacting therewith to form a capsule wall (e.g., polyol or polyamine) in an aqueous medium or an oil medium to be encapsulated, emulsifying such materials in water and heating to induce a polymer forming reaction at the

interface of oil droplets, thereby forming a microcapsule wall. A polyurea can be generated even when dispensing with the addition of the second material.

[0087]

In the invention, the polymer substance forming the microcapsule wall is preferably at least one selected from polyurethane and polyurea.

[0088]

Below, a method of preparing microcapsules will be explained using an example of microcapsules (with a polyurea/polyurethane wall) containing a diazo compound.

[0089]

In the above-described method, firstly, a diazo compound is dissolved or dispersed in a high-boiling organic solvent to prepare an oil phase constituting a core of the microcapsules. In the invention, the high-boiling organic solvent is preferably employed in a proportion of 0.25 to 10 parts by mass per 1 part by mass of the diazo compound, more preferably in a proportion of 0.5 to 5 parts by mass. When the amount of the high-boiling organic solvent to be used is less than 0.25 parts by mass, the background fog tends to be at a low level and

when the amount of the high-boiling organic solvent is more than 10 parts by mass, sufficiently high color density may not be obtained. When preparing the oil phase, a polyisocyanate is added as a wall material.

[0090]

The high-boiling solvent can be alkylbiphenyl, alkylnaphthalene, alkyldiphenylethane, alkyldiphenylmethane, chlorinated paraffin, tricresyl phosphate, a maleic acid ester, an adipic acid ester or a phthalic acid ester. Such high-boiling solvents can be employed in combination of two or more kinds.

[0091]

In the preparation of the oil phase, the diazo compound is usually dissolved in a core oil and used. However, if the diazo compound has a low solubility in the high-boiling solvent, it is preferable to employ in combination a low-boiling organic solvent (i.e., with a boiling point of 100°C or lower) with a high solubility as an auxiliary solvent. The low-boiling organic solvent can be ethyl acetate, butyl acetate, methylene chloride, tetrahydrofuran or acetone. In such a case, the low-boiling solvent evaporates during the capsule forming reaction and does not remain in the completed capsules,

therefore, there is no particular limitation on the amount used.

[0092]

It is preferred that the diazo compound has an appropriate solubility in the low-boiling organic solvent and the high-boiling organic solvent mentioned above. More specifically, it is preferred that the diazo compound has a solubility of 5% or higher in such solvents and a solubility of 1% or less in water.

[0093]

On the other hand, for an aqueous phase to be used, an aqueous solution is used in which a water-soluble polymer is dissolved, and the aforementioned oil phase is added therein and emulsified with a high-speed rotation means such as a homogenizer. The water-soluble polymer also functions as a dispersant for homogenizing and facilitating the dispersion and stabilizing the emulsified aqueous solution. Further, in order to achieve further uniform emulsification and stabilization, a surfactant may be added to at least one of the oil phase and the aqueous phase. In this regard, as a surfactant, known emulsifying surfactants can be used. Further, when a surfactant is added, the amount of the surfactant is preferably 0.1 to

5% based on the entire mass of the oil phase, and particularly preferably 0.5 to 2 %.

[0094]

The water-soluble polymer, to be added to the aqueous solution used in the emulsification, preferably has a solubility of 5 or higher in water at the emulsification temperature. Specific examples of the water-soluble polymer include polyvinyl alcohol and a modification thereof, poly acrylamide and a derivative thereof, an ethylene-vinyl acetate copolymer, a styrene-maleic anhydride copolymer, an ethylene-maleic anhydride copolymer, an isobutylene-maleic anhydride copolymer, polyvinylpyrrolidone, an ethylene-acrylic acid copolymer, a vinyl acetate-acrylic acid copolymer, carboxymethyl cellulose, methyl cellulose, casein, gelatin, a starch derivative, gum Arabic and sodium alginate.

[0095]

The water-soluble polymer preferably has little to no reactivity with an isocyanate compound to be added as a wall material, and, for example in a material having a reactive amino group in a molecular chain such as gelatin, it is necessary to eliminate the reactivity by a denaturing or the like in advance.

[0096]

The aforementioned polyisocyanate group-having compound is preferably a compound having a tri- or higher-functional isocyanate groups, but a bi-functional isocyanate compound may be used in combination therewith. Specific examples of a diisocyanate main material include xylene diisocyanate and hydrogenated products thereof, hexamethylene diisocyanate, tolylene diisocyanate and hydrogenated products thereof, an isophoronediiisocyanate, or dimers or trimers of these (e.g., biuret or isocyanurate) or a polyfunctional adduct with a polyol such as trimethylol propane, and a formalin condensate of benzene isocyanate.

[0097]

The amount of the polyisocyanate mentioned above is determined so that the microcapsules have an average particle size of 0.3 to 12 μm and a capsule wall thickness of 0.01 to 0.3 μm . The diameter of the dispersed particles is generally about 0.2 to 10 μm . A polymerization reaction of polyvalent isocyanate takes place at the interface between the oil phase and the aqueous phase in the emulsion, to form a polyurea wall.

[0098]

Further, a polyol or a polyamine may be added in the aqueous phase or in the hydrophobic solvent, thereby reacting with the polyvalent isocyanate and being utilized as one of the materials for the microcapsule wall. In the reaction, it is preferable to maintain a high reaction temperature or to add an appropriate polymerization catalyst in order to increase the reaction speed.

[0099]

Specific examples of polyol and/or polyamine include propylene glycol, glycerin, trimethylol propane, triethanolamine, sorbitol, and hexamethylenediamine. When adding a polyol a polyurethane wall is formed.

[0100]

Polyisocyanate, polyol, reaction catalyst, and polyamine forming a part of the wall material are described in detail in a reference (*Polyurethane Handbook*, Nikkan Kogyo Shimbun-sha, edited by Keiji Iwata (1987)).

[0101]

The emulsifying operation can be executed with a known emulsifying apparatus such as a homogenizer, a manton-Goulin, an ultrasonic disperser, a dissolver or a

KD mill. After the emulsification, the emulsion is heated to 30 to 70°C in order to accelerate the capsule wall forming reaction. Also, during the reaction, it is necessary to add water, so as to lower the probability of mutual collision of the microcapsules or to execute sufficient agitation, in order to prevent mutual coagulation of the microcapsules.

[0102]

During the reaction, another dispersion for preventing coagulation may be added. Generation of carbon oxide gas is observed with the progress of the polymerization reaction, and the end point of the capsule wall forming reaction can be judged approximately based on the end of the gas generation. Usually, the desired microcapsules containing the diazo compound can be obtained by a reaction of several hours.

[0103]

(Configuration of thermal recording material)

In the present invention, the thermal recording material may be provided with a plurality of laminated thermal recording layers. A multi-color thermal recording material can be obtained by changing the color hues of the photo-fixable thermal recording layers. The layer

configuration in such a case is not particularly restricted. However, it is preferred that the multi-color thermal recording material has superposed thereon photo-fixable thermal recording layers (two layers) in which two diazonium salt compounds having different photosensitive wavelengths are respectively combined with coupler compounds capable of forming different color hues by reaction under heating with the respective diazonium salt compounds, and a photo-fixable thermal recording layer in which an electron donating colorless dye and an electron accepting compound are combined. More specifically it has, on a support, a first photo-fixable thermal recording layer including an electron donating colorless dye and an electron accepting compound; a second photo-fixable thermal recording layer including a diazonium salt compound having a maximum absorption wavelength of 365 ± 40 nm and a coupler compound capable of forming a color by reaction under heating with the diazonium salt compound; and a third photo-fixable thermal recording layer including a diazonium salt compound having a maximum absorption wavelength of 425 ± 40 nm and a coupler compound capable of forming a color by reaction under heating with the diazonium salt compound. In this example, full-color image recording is possible by selecting three primary colors in the subtractive color

mixing, namely yellow, magenta and cyan, for the color hues to be formed in these photo-fixable thermal recording layers.

[0104]

The recording method in this multi-color thermal recording material is executed as follows. First, the third photo-fixable thermal recording layer is heated to execute color formation by the diazonium salt and the coupler, which are in the layer. Then, after irradiation with light of a wavelength of 425 ± 40 nm to decompose the unreacted diazonium salt compound contained in the third photo-fixable thermal recording layer, heat sufficient for color formation in the second photo-fixable thermal recording layer is added thereto, thereby causing color formation by the diazonium salt compound and the coupler, which are in the layer. At this time, the third photo-fixable thermal recording layer is also simultaneously strongly heated, but no further color formation takes place because the diazonium salt compound is already decomposed and the color forming ability is lost. Then, irradiation with light of a wavelength of 365 ± 40 nm is executed to decompose the diazonium salt compound included in the second photo-fixable thermal recording layer, and heat sufficient for color formation in the first photo-

fixable thermal recording layer is added, thereby forming a color therein. At the same time, the third and second photo-fixable thermal recording layers are also strongly heated, but no further color formation takes place because the diazonium compounds are already decomposed so that the color forming ability is lost.

[0105]

In the invention, in order to further improve light fastness, known antioxidants as shown in the following patent documents may be added to the thermal recording material.

Examples of such antioxidants include those described in EP-A No. 310551, GP-A No. 3435443, EP-A No. 310552, JP-A No. 3-121449, EP-A No. 459416, JP-A Nos. 2-262654, 2-71262 and 63-163351, USP No. 4,814,262, JP-A Nos. 54-48535, 5-61166 and 5-119449, USP No. 4,980,275, JP-A Nos. 63-113536 and 62-262047, EP-A Nos. 223739, 309402 and 309401. Specific examples of the antioxidant are shown below.

[0106]

It is also effective to use various additives already known for thermal recording materials or pressure-sensitive recording materials. Examples of such

antioxidants include those described in JP-A Nos. 60-125470, 60-125471, 60-125472, 60-287485, 60-287486, 60-287487, 62-146680, 60-287488, 62-282885, 63-89877, 63-88380, 63-088381, 01-239282, 04-291685, 04-291684, 05-188687, 05-188686, 05-110490, 05-1108437, 05-170361, 63-203372, 63-224989, 63-267594, 63-182484, 60-107384, 60-107383, 61-160287, 61-185483, 61-211079, 63-251282 and 63-051174, JP-B Nos. 48-043294 and 48-033212.

[0107]

A conventional binder resin can be used in the thermal recording layer, but is preferable to use polyvinyl alcohol. A water-soluble polymer such as gelatin or a polymer latex can also be employed.

[0108]

<Light transmittance control layer>

In the thermal recording material of the invention, a light transmittance control layer is preferably provided in order to improve light fastness.

The light transmittance control layer may include an ultraviolet absorber precursor, which does not function as an ultraviolet absorber prior to irradiation with light of a wavelength region required for fixation of a photo-fixable thermal recording layer, hence the layer shows a

high optical transmittance. Also at the fixation of the photo-fixable thermal recording layer, the light transmittance control layer sufficiently transmits the light of the wavelength region required for fixation, and also shows a high light transmittance in the visible region, thereby not hindering the fixation of the thermal recording layer. This ultraviolet absorber precursor is preferably included in microcapsules. The compound to be included in the light transmittance control layer can be those described in JP-A No. 9-1928.

[0109]

After irradiation with light of the wavelength region required for the fixation of the thermal recording layer by light irradiation, the ultraviolet absorber precursor is reacted by light or heat to become functionable as an ultraviolet absorber. Most of the light of the ultraviolet wavelength region required for the fixation is absorbed by the ultraviolet absorber, whereby the transmittance is lowered. Therefore the light fastness of the thermal recording material is improved, but the transmittance for visible light remains substantially unchanged because the ultraviolet absorber lacks an absorbing effect for visible light.

The light transmittance control layer can be

provided in at least one layer in the thermal recording material. It is most preferably provided between a thermal recording layer and an outermost protective layer. The light transmittance control layer may also be constructed so as to serve as a protective layer. Characteristics of the light transmittance control layer can be arbitrarily selected according to the characteristics of the thermal recording layer.

[0110]

The coating solution for forming the light transmittance control layer (light transmittance control layer coating solution) can be obtained by mixing the components explained in above. The light transmittance control layer can be formed by coating the thus-obtained coating solution with a known coating method such as bar coating, air knife coating, blade coating or curtain coating. The light transmittance control layer may be coated simultaneously with the thermal recording layer, or coated and formed on the thermal recording layer after the coating solution for forming the thermal recording layer is coated and dried.

The dry coating amount of the light transmittance control layer is preferably within a range of 0.8 to 4.0 g/m².

[0111]

<Intermediate layer>

When superposing multiple thermal recording layers, an intermediate layer is preferably provided between the thermal recording layers. The intermediate layer may contain, as in the protective layer, various binders, a pigment, a lubricant, a surfactant, a dispersant, a fluorescent whitening agent, a metal soap, an ultraviolet absorber, etc. The binder can be similar to those used in the protective layer. Also, in order to increase the film strength of the thermal recording material, a hardening agent such as a crosslinking agent such as boric acid capable of causing a crosslinking reaction with the binder of the protective layer can be added in a coating solution for the intermediate layer.

[0112]

<Support>

Examples of materials for the support include polyethylene terephthalate (PET), polyethylene naphthalate (PEN), triacetyl cellulose (TAC), paper, paper laminated with a plastic resin, or synthetic paper. In order to obtain a transparent thermal recording material, it is necessary to use a transparent support, such as a

synthetic polymer film. Examples of these include polyester films such as polyethylene terephthalate or polybutylene terephthalate, and cellulose triacetate films or polyolefin films such as polypropylene or polyethylene.

[0113]

These supports may be used individually or in a mutually adhered state. The synthetic polymer film preferably has a thickness of 25 to 300 μm , and more preferably of 100 to 250 μm .

[0114]

The synthetic polymer film may be colored into arbitrary color hues. Coloring methods for the polymer film include a method of blending a dye in a resin in advance and then forming into a film shape, or a method of preparing a coating solution by dissolving a dye in an appropriate solvent and coating and drying the solution on a transparent colorless resinous film, by a known coating method such as gravure coating, roller coating or wire bar coating. Among these, there is preferred a support obtained by molding a polyester resin such as PET or PEN, in which a blue dye is blended, into a film shape and applying thereto heat-resistance treatment, drawing treatment and antistatic treatment.

[0115]

The thermal recording layer, protective layer, light transmittance control layer, intermediate layer, etc. can be formed, on a support, by coating with a known coating method such as blade coating, air knife coating, gravure coating, roll coating, spray coating, dip coating or bar coating, and then dried.

[0116]

[EXAMPLES]

Below, the thermal recording material of the present invention will be further clarified with examples, but the invention is not limited by such examples. In the following description, "part" and "%" respectively mean "part by mass" and "% by mass", unless otherwise specified.

[0117]

[Example 1]

<Preparation of phthalated gelatin aqueous solution>

32 parts of phthalated gelatin (trade name: MGP gelatin, manufactured by Nippi Collagen Co., Ltd.); 0.9143 parts of 1,2-benzothiazolin-3-one (3.5% methanol solution, manufactured by Daito Chemical Industries,

Ltd.); and 367.1 parts of ion-exchanged water were mixed and dissolved at 40°C to obtain a phthalated gelatin aqueous solution.

[0118]

<Preparation of alkali-treated aqueous gelatin solution>

25.5 parts of alkali-treated low-ion content gelatin (trade name: #750 gelatin, manufactured by Nitta Gelatin Inc.); 0.7286 parts of 1,2-benzothiazolin-3-one (3.5% methanol solution, manufactured by Daito Chemical Industries, Ltd.); 0.153 parts of calcium hydroxide; and 143.6 parts of ion-exchanged water were mixed and dissolved at 50°C to obtain an alkali-treated gelatin aqueous solution for preparing an emulsion.

[0119]

(1) Preparation of coating solution for yellow thermal recording layer

<Preparation of diazonium compound containing microcapsule solution (a) >

2.2 parts of a following diazonium salt compound (A) (maximum absorption wavelength 420 nm); 2.2 parts of a following diazonium compound (B) (maximum absorption wavelength 420 nm); 4.8 parts of monoisopropylbiphenyl, 4.0 parts of diphenyl phthalate and 0.4 parts of diphenyl-

(2,4,6-trimethylbenzoyl)phosphin oxide (trade name: Lucirin TPO, manufactured by BASF Japan Co.) were added to 16.1 parts of ethyl acetate, and dissolved uniformly by heating at 40°C. To this mixture, 8.6 parts of a mixture of xylylene diisocyanate/trimethylolpropane adduct and xylylene diisocyanate/bisphenol-A adduct (trade name: Takenate D119N (50% solution in ethyl acetate), manufactured by Mitsui-Takeda Chemicals, Inc.) were added as a capsule wall material and were uniformly stirred to obtain a mixture (I).

[0120]

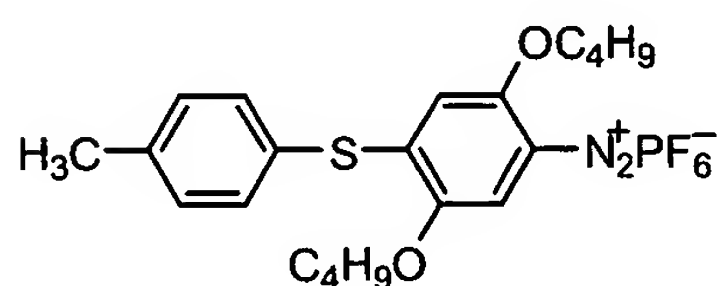
Separately, 16.3 parts of ion-exchanged water and 0.34 parts of 50% Scrapp AG-8 manufactured by Nippon Seika Co. were added to 58.6 parts of the above-mentioned phthalated gelatin aqueous solution to obtain a mixture (II).

Mixture (I) was added to mixture (II), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. 20 parts of water were added to the obtained emulsion and mixed uniformly, and then subjected to an encapsulation reaction for 3 hours while stirring 40°C to eliminate ethyl acetate. Thereafter, 4.1 parts of an ion exchange resin (trade name: Amberlite IRA68, manufactured by Organo Corp.) and 8.2 parts of an

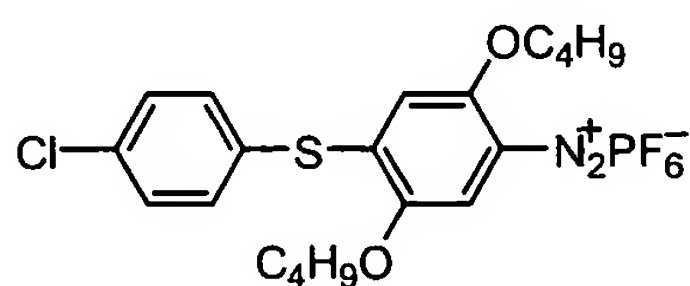
ion exchange resin (trade name: Amberlite IRC50, manufactured by Organo Corp.) were added and the mixture was further stirred for 1 hour. Thereafter, the ion exchange resin was eliminated by filtration, and the capsule solution was subjected to an adjustment of concentration so as to obtain a solid content of 20.0%, thereby obtaining a diazonium salt compound containing microcapsule solution (a). The result of measurement with a particle size distribution measuring apparatus (trade name: LA-700, manufactured by Horiba Co.) indicated that the obtained microcapsules had a median diameter of 0.36 μm .

[0121]

Diazonium compound (A)



Diazonium compound (B)



[0122]

<Preparation of coupler compound emulsion (a)>

9.9 parts of a following coupler compound (C); 9.9 parts of triphenylguanidine (manufactured by Hodogaya Chemical Co., Ltd.); 20.8 parts of 4,4'-(m-

phenylenediisopropylidene)-diphenol (trade name: Bisphenol M, manufactured by Mitsui Petrochemicals Inc.); 3.3 parts of 3,3,3',3'-tetramethyl-5,5',6,6'-tetra(1-propyloxy)-1,1'-spirobisindane; 13.6 parts of 4-(2-ethylhexyloxy)benzenesulfonic acid amide (manufactured by Manac Incorporated.); 6.8 parts of 4-n-pentyloxybenzenesulfonic acid amide (manufactured by Manac Inc.); and 4.2 parts of calcium dodecylbenzenesulfonate (trade name: Pionin A-41-C (70% methanol solution), manufactured by Takemoto Oil & Fat Co., Ltd.) were dissolved in 33.0 parts of ethyl acetate to obtain a mixture (III).

[0123]

Separately, 206.3 parts of the above-mentioned alkali-treated gelatin aqueous solution were mixed with 107.3 parts of ion-exchanged water to obtain a mixture (IV).

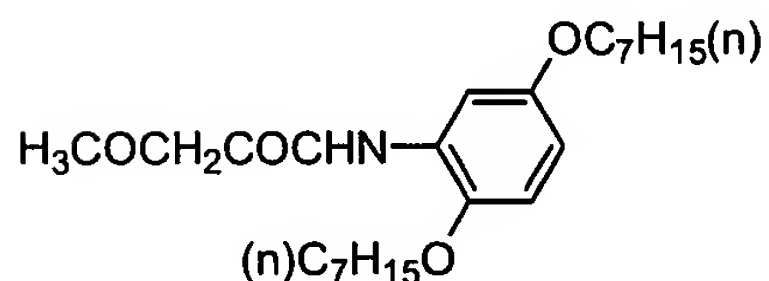
The mixture (III) was added to the mixture (IV), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion of the coupler compound was heated under reduced pressure to eliminate ethyl acetate, and subjected to an adjustment of concentration so as to obtain a solid content of 26.5%. The result of measurement with a particle size

distribution measuring apparatus (trade name LA-700, manufactured by Horiba Co.) indicated that the obtained emulsion of the coupler compound had a median diameter of 0.21 μm .

Further, 9 parts of SBR latex (trade name: SN-307 (48% liquid), manufactured by Sumika ABS Latex Co.), adjusted to a concentration of 26.5%, were added to 100 parts of the aforementioned emulsion of coupler compound and were uniformly stirred to obtain a coupler compound emulsion (a).

[0124]

Coupler compound (C)



[0125]

<Preparation of coating solution (a)>

The diazonium salt containing microcapsule solution (a) and the emulsion (a) of the coupler compound were mixed such that the mass ratio of the included coupler compound/diazonium compound became 2.2/1, thereby

obtaining a coating solution (a).

[0126]

(2) Preparation of solution for magenta recording layer

<Preparation of diazonium salt containing microcapsule solution (b)>

In 15.1 parts of ethyl acetate, 2.8 parts of a following diazonium compound (D) (maximum absorption wavelength 365 nm); 3.8 parts of diphenyl phthalate; 3.9 parts of phenyl 2-benzoyloxybenzoate ester; 5.2 parts of a following ester compound (trade name: Light Ester TMP, manufactured by Kyoei Yushi Kagaku Co.); and 0.1 parts of calcium dodecylbenzenesulfonate (trade name: Pionin A-41-C, 70% methanol solution, manufactured by Takemoto Oil & Fat Co., Ltd.) were added, and uniformly dissolved by heating. To this mixture, 2.5 parts of a mixture of xylylene diisocyanate/trimethylolpropane adduct and xylylene diisocyanate/bisphenol-A adduct (trade name: Takenate D119N (50% ethyl acetate solution), manufactured by Mitsui Takeda Chemicals, Inc.) and 6.8 parts of a xylylene diisocyanate/trimethylolpropane adduct (trade name: Takenate D110N (75% ethyl acetate solution) manufactured by Mitsui Takeda Chemicals, Inc.) were added as capsule wall materials and uniformly stirred to obtain a mixture (V).

[0127]

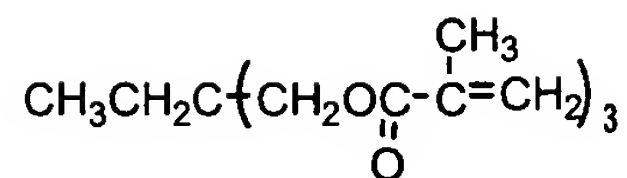
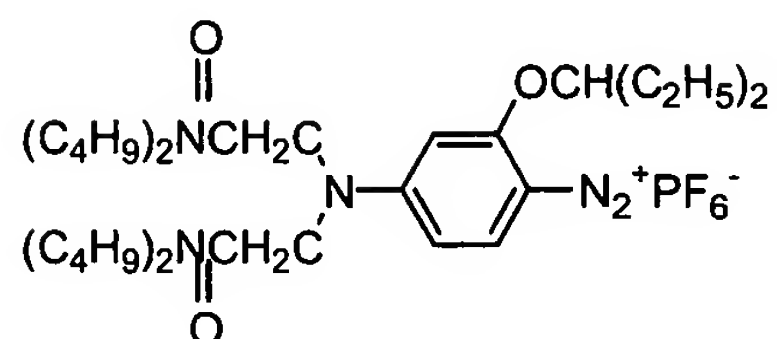
Separately, 21.0 parts of ion-exchanged water were added to 55.3 parts of the above-mentioned phthalated gelatin aqueous solution to obtain a mixture (VI).

The mixture (V) was added to the mixture (VI), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion was mixed uniformly with 24 parts of water, and then subjected to an encapsulation reaction for 3 hours while stirring at 40°C to eliminate ethyl acetate. Thereafter, 4.1 parts of an ion exchange resin (trade name: Amberlite IRA68, manufactured by Organo Corp.) and 8.2 parts of an ion exchange resin (trade name: Amberlite IRC50, manufactured by Organo Corp.) were added and the mixture was further stirred for 1 hour. Thereafter, the ion exchange resin was eliminated by filtration, and the capsule solution was subjected to an adjustment of concentration so as to obtain a solid content of 20.0%, thereby obtaining a diazonium salt containing microcapsule solution (b). The result of measurement with a particle size distribution measuring apparatus (trade name: LA-700, manufactured by Horiba Co.) indicated that the obtained microcapsules had a median diameter of 0.43 μm .

[0128]

Diazonium compound (D)

Ester compound



[0129]

<Preparation of coupler compound emulsion (b)>

In 36.9 parts of ethyl acetate, 11.9 parts of a following coupler compound (E); 14.0 parts of triphenylguanidine (manufactured by Hodogaya Chemical Co., Ltd.); 14.0 parts of 4,4'-(m-phenylenediisopropylidene)-diphenol (trade name: Bisphenol M, manufactured by Mitsui Petrochemicals Inc.); 14.0 parts of 1,1-(p-hydroxyphenyl)-2-ethylhexane; 3.5 parts of 3,3,3',3'-tetramethyl-5,5',6,6'-tetra(1-propyloxy)-1,1'-spirobisindane; 3.5 parts of a following compound (G); 1.7 parts of tricresyl phosphate; 0.8 parts of diethyl maleate; and 4.5 parts of calcium dodecylbenzenesulfonate (trade name: Pionin A-41-C (70% methanol solution), manufactured by Takemoto Oil & Fat Co., Ltd.) were dissolved to obtain a mixture (VII).

[0130]

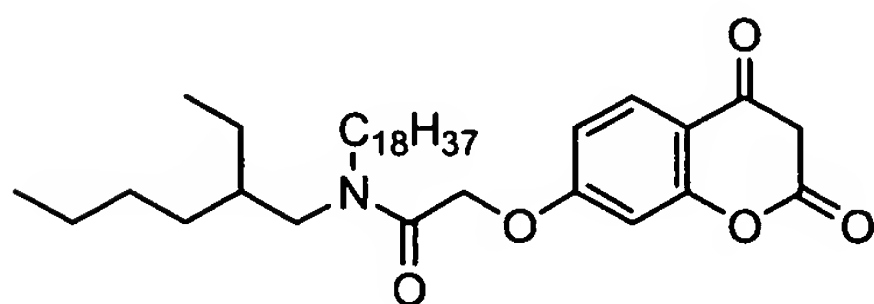
Separately, 206.3 parts of the above-mentioned

alkali-treated gelatin aqueous solution were mixed with 107.3 parts of ion-exchanged water to obtain a mixture (VIII).

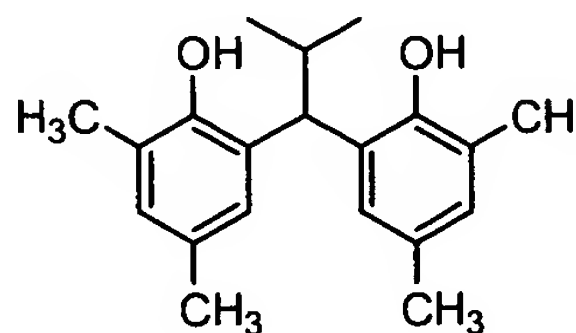
Mixture (VII) was added to mixture (VIII), and emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion of the coupler compound was heated under reduced pressure to eliminate ethyl acetate, and subjected to an adjustment of concentration so as to obtain a solid content of 24.5%, thereby obtaining an emulsion (b) of the coupler compound. The result of measurement with a particle size distribution measuring apparatus (trade name LA-700, manufactured by Horiba Co.) indicated that the obtained emulsion of the coupler compound had a median diameter of 0.22 μm .

[0131]

Coupler compound (E)



Compound (G)



[0132]

<Preparation of coating solution (b) >

The diazonium salt containing microcapsule solution (b) and the emulsion (b) of the coupler compound were mixed such that the mass ratio of the included coupler compound/diazonium compound became 3.5/1. Further, an aqueous solution (5%) of polystyrenesulfonic acid (partially neutralized with potassium hydroxide) was mixed in an amount of 0.2 parts to 10 parts of the capsule solution, thereby obtaining a coating solution (b) for the thermal recording layer.

[0133]

(3) Preparation of solution for cyan thermal recording layer

<Preparation of electron donating dye precursor containing microcapsule solution (c)>

In 18.1 parts of ethyl acetate, 7.6 parts of a following electron donating dye (H); 8.0 parts of a mixture of 1-methylpropylphenyl-phenylmethane and 1-(1-methylpropyl-phenyl)-2-phenylethane (trade name: Hysol SAS-310, manufactured by Japan Oil Co, Ltd.); and 8.0 parts of a following compound (I) (trade name: Irgaperm 2140, manufactured by Ciba-Geigy Inc.) were added, heated and uniformly dissolved by heating. To this mixture, 7.2 parts of a xylylene diisocyanate/trimethylolpropane adduct (trade name: Takenate D110N (75% ethyl acetate solution)

manufactured by Mitsui Takeda Chemicals, Inc.) and 5.3 parts of polymethylene polyphenyl polyisocyanate (trade name: Millionate MR-200, manufactured by Nippon Polyurethane Industries, Co., Ltd.) were added as capsule wall materials and uniformly stirred to obtain a mixture (IX) .

[0134]

Separately, 9.5 parts of ion-exchanged water; 0.17 parts of 50% Scrapp AG-8, manufactured by Nippon Seika Co.; and 4.3 parts of sodium dodecylbenzenesulfonate (10% aqueous solution) were added to 28.8 parts of the above-mentioned phthalated gelatin aqueous solution to obtain a mixture (X) .

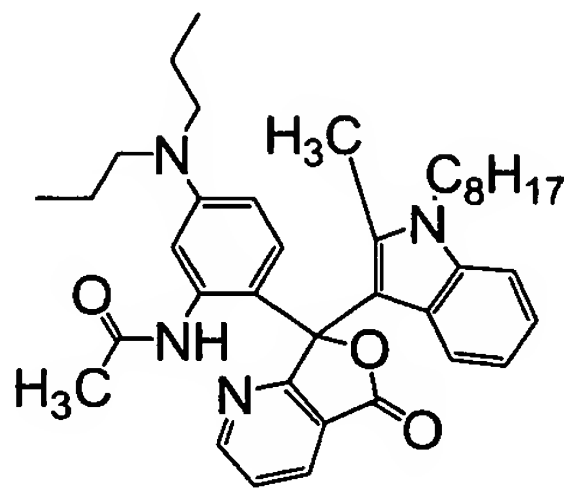
Mixture (IX) was added to mixture (X), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion was mixed uniformly with 50 parts of water and 0.12 parts of tetraethylene pentamine, and was subjected to an encapsulation reaction for 3 hours while stirring at 65°C to eliminate ethyl acetate, and the concentration was adjusted as to obtain a solid concentration of 33% in the liquid, thereby obtaining a microcapsule solution. The result of measurement with a particle size distribution measuring apparatus (trade name LA-700, manufactured by

Horiba Co.) indicated that the obtained microcapsules had a median diameter of 1.00 μm .

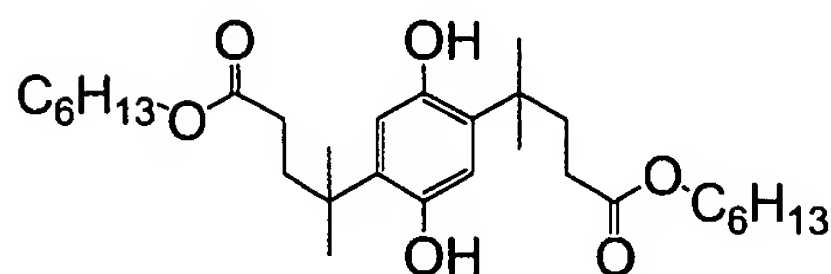
Further, 3.7 parts of a 25% aqueous solution of sodium dodecylbenzenesulfonate (trade name: NEOPELEX F-25, manufactured by Kao Corp.) and 4.2 parts of a fluorescent whitening agent containing a 4,4'-bistriazinyl-aminostylbene-2,2'-disulfon derivative (trade name: Kaycoll BXNL, manufactured by Nippon Soda Co., Ltd.) were added to 100 parts of the microcapsule solution and uniformly stirred to obtain a electron donating dye precursor containing microcapsule dispersion (c).

[0135]

[Electron donating dye processor (H)]



Compound (I)



[0136]

<Preparation of electron accepting compound dispersion (c)>

30.1 parts of ion-exchanged water; 15 parts of 4,4'-(p-phenylenediisopropylidene)diphenol (trade name: bisphenol P, manufactured by Mitsui Petrochemical Co.); and 3.8 parts of a 2% aqueous solution of sodium 2-ethylhexylsuccinate were added to 11.3 parts of the phthalated gelatin aqueous solution and dispersed overnight with a ball mill to obtain a dispersion. The dispersion had a solid content of 26.6%. 100 parts of the dispersion had added thereto 45.2 parts of the alkali-treated gelatin aqueous solution, and was then stirred for 30 minutes, after which ion-exchanged water was added so as to obtain a solid content of 23.5% thereby obtaining an electron accepting compound dispersion (c).

[0137]

<Preparation of coating solution (c)>

The electron donating dye precursor containing microcapsule solution (c) and the electron accepting compound dispersion (c) were mixed such that the mass ratio of the electron accepting compound/electron donating dye precursor became 10/1, thereby obtaining a coating

solution (c).

[0138]

(4) Preparation of coating solution for intermediate layer

100.0 parts of alkali-treated low ion content gelatin (trade name: #750 gelatin, manufactured by Nitta Gelatin Inc.); 2.857 parts of 1,2-benzothiazolin-3-one (3.5 % methanol solution, manufactured by Daito Chemical Industries, Ltd.); 0.5 parts of calcium hydroxide; and 521.643 parts of ion-exchanged water were mixed and dissolved at 50°C to obtain an aqueous gelatin solution for preparing an intermediate layer.

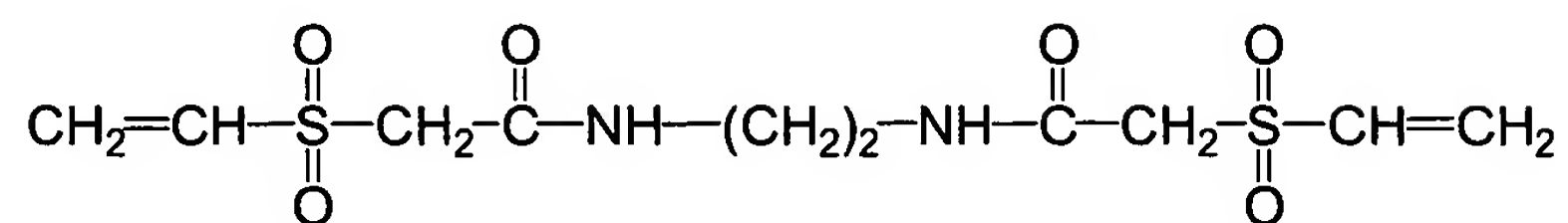
[0139]

10.0 parts of the gelatin aqueous solution for preparing the intermediate layer; 0.05 parts of sodium (4-nonylphenoxytrioxyethylene)butylsulfonate (2.0% aqueous solution, manufactured by Sankyo Chemicals Co., Ltd.); 0.19 parts of a 5% aqueous solution of polystyrenesulfonic acid (partially neutralized with potassium hydroxide); 2.7 parts of boric acid (4.0% aqueous solution); 3.42 parts of a 4% aqueous solution of a following compound (J) (manufactured by Wako Pure Chemical Ltd.); 1.13 parts of a 4% aqueous solution of a following compound (J') (manufactured by Wako Pure Chemical Ltd.); and 0.67 parts

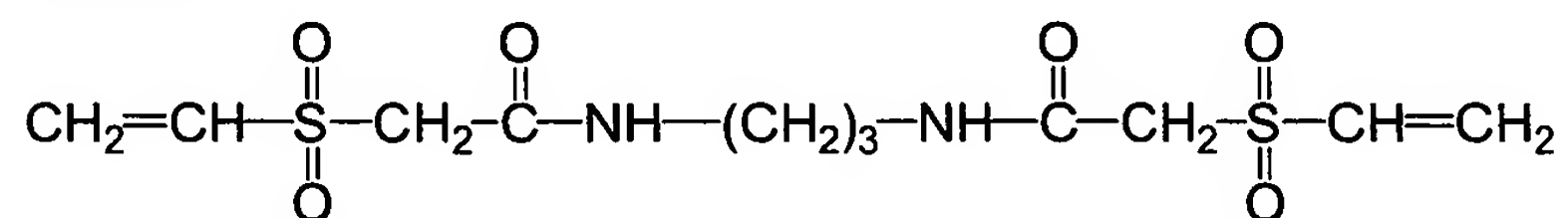
of ion-exchanged water were mixed to obtain a coating solution for the intermediate layer.

[0140]

Compound (J)



Compound (J')



[0141]

(5) Preparation of coating solution for optical transmittance control

<Preparation of microcapsule solution of ultraviolet absorber precursor>

14.5 parts of [2-allyl-6-(2H-benzotriazol-2-yl)-4-t-octylphenyl]benzenesulfonate as an ultraviolet absorber precursor; 5.0 parts of 2,2'-t-octylhydroquinone; 1.9 parts of tricresyl phosphate; 5.7 parts of α-methylstyrene dimer (trade name: MSD-100, manufactured by Mitsui Chemicals Inc.); and 0.55 parts of calcium dodecylbenzenesulfonate (trade name: Pionin A-41-C, (70% methanol solution) manufactured by Takemoto Oil & Fat Co.,

Ltd) were uniformly dissolved in 71 parts of ethyl acetate. To this mixture, 54.7 parts of a xylylene diisocyanate/trimethylolpropane adduct (trade name: Takenate D110N (75% ethyl acetate solution), manufactured by Mitsui Takeda Chemicals, Inc.) were added as a capsule wall material, and the mixture was uniformly stirred to obtain a mixture (VII) of the ultraviolet absorber precursor.

[0142]

Separately, 8.9 parts of a 30% aqueous solution of phosphoric acid, and 532.6 parts of ion-exchanged water were mixed in 52 parts of itaconic acid-modified polyvinyl alcohol (trade name: KL-318, manufactured by Kuraray Co., Ltd) to obtain a polyvinyl alcohol (PVA) aqueous solution for a microcapsule solution of the ultraviolet absorber precursor.

[0143]

The aforementioned mixture (VII) of the ultraviolet absorber precursor was added to 516.06 parts of the aqueous PVA solution for the ultraviolet absorber precursor microcapsule solution, and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 20°C. The obtained emulsion was mixed uniformly with 254.1

parts of ion-exchanged water, and was subjected to an encapsulation reaction for 3 hours while stirring at 40°C. Thereafter, 94.3 parts of an ion exchange resin (trade name: Amberlite MB-3, manufactured by Organo Corp.) were added and the mixture was further stirred for 1 hour. Thereafter the ion exchange resin was eliminated by filtration, and the capsule solution was subjected to an adjustment of concentration so as to obtain a solid content of 13.5%. The result of a particle size measurement with a particle size distribution measuring apparatus (trade name: LA-700, manufactured by Horiba Co.) indicated that the obtained microcapsules had a median diameter of $0.23 \pm 0.05 \mu\text{m}$. 859.1 parts of the microcapsule solution were mixed with 2.416 parts of carboxy-modified styrene-butadiene latex (trade name: SN-307 (48% aqueous solution), manufactured by Sumitomo Nogtakku) and 39.5 parts of ion-exchanged water to obtain a microcapsule solution of the ultraviolet absorber precursor.

[0144]

<Preparation of coating solution for optical transmittance control layer>

1000 parts of the microcapsule solution of the ultraviolet absorber precursor; 7.75 parts of a 4% aqueous

solution of sodium hydroxide; and 73.39 parts of sodium (4-nonylphenoxytrioxyethylene)butylsulfonate (2.0% aqueous solution, manufactured by Sankyo Chemicals Co., Ltd.) were mixed to obtain a coating solution for the light transmittance control layer.

[0145]

(6) Preparation of coating solution for protective layer

<Preparation of polyvinyl alcohol solution for protective layer>

150 parts of a vinyl alcohol-alkylvinyl ether copolymer (trade name: EP-130, manufactured by Denka Corp.); 7.5 parts of a mixture of sodium alkylsulfonate and a polyoxyethylene alkyl ether phosphoric acid ester (trade name: Neoscore CM-57 (54% aqueous solution), manufactured by Toho Chemical Industries, Co., Ltd.); 7.05 parts of an ethylene oxide adduct of acetylenediol (trade name: Dinol 604, manufactured by Air Products Japan, Inc.); 7.05 parts of a silicone surfactant (trade name: SYLGARD 309, manufactured by Toray-Dow Corning Silicone Ltd.); and 3592 parts of ion-exchanged water were mixed and dissolved for 1 hour at 90°C to obtain a uniform polyvinyl alcohol solution for the protective layer.

[0146]

<Preparation of pigment dispersion for protective layer>

0.2 parts of an anionic special polycarboxylic acid polymer activator (trade name: Poise 532A (40% aqueous solution), manufactured by Kao Corp.) and 11.8 parts of ion-exchanged water were mixed with 8 parts of barium sulfate (trade name: BF-21F, barium sulfate content 93% or higher, manufactured by Sakai Chemical Industries, Co.) and dispersed in a Dyno mill to prepare a pigment dispersion for the protective layer. The result of a measurement with a particle size distribution measuring apparatus (trade name: LA-700, manufactured by Horiba Co.) indicated that the dispersion had a median diameter of 0.15 μm .

82.0 parts of the barium sulfate dispersion were added with 18.4 parts of colloidal silica (trade name: Snowtex-O, 20% aqueous dispersion, manufactured by Nissan Chemical Industries, Ltd., average particle size 20 nm) to obtain the desired pigment dispersion for the protective layer.

[0147]

<Preparation of matting agent dispersion for protective layer>

3.81 parts of an aqueous dispersion of 1-2-benzisothiazolin-3-one (trade name: PROXEL B.D,

manufactured by I.C.I. Ltd.) and 1976.19 parts of ion-exchanged water were mixed in 220 parts of wheat starch (trade name: Wheat starch S, manufactured by Shinshin Shokuryo Kogyo Co.) and dispersed uniformly to obtain a dispersion of the matting agent for the protective layer.

[0148]

<Preparation of coating solution for protective layer>

50 parts of sodium (4-nonylphenoxytrioxyethylene) butylsulfonate (2.0% aqueous solution, manufactured by Sankyo Chemicals, Co.); 61.2 parts of the pigment dispersion for the protective layer; 16.65 parts of the dispersion of the matting agent for the protective layer; 48.7 parts of a zinc stearate dispersion (trade name: Himicron LIII, 21% aqueous solution, manufactured by Chukyo Yushi Co.); 4.8 parts of zirconium ammonium carbonate (trade name: Zircosol AC7, 13% aqueous solution, manufactured by Newtex Co.); and 280 parts of ion-exchanged water were uniformly mixed in 1000 parts of the polyvinyl alcohol solution for the protective layer to obtain a coating solution for the protective layer.

[0149]

(7) Preparation of support

<Preparation of coating solution for undercoating layer>

40 parts of enzyme-decomposed gelatin (average molecular weight: 10000, viscosity by PAGI method: 1.5 mPa.s (15 mP), jelly strength by PAGI method: 20 g) were mixed with 60 parts of ion-exchanged water and dissolved while stirring at 40°C to obtain an aqueous gelatin solution for the undercoat layer.

Separately, 8 parts of water-swelling synthetic mica (aspect ratio: 1000, trade name: Somashif ME100, manufactured by Cope Chemical Inc.) were mixed with 92 parts of water and subjected to wet dispersion in a visco mill to obtain a mica dispersion with an average particle size of 2.0 μm . The mica dispersion had water added thereto so as to obtain a mica concentration of 5% and was uniformly mixed to obtain a desired mica dispersion.

[0150]

To 100 parts of the aforementioned 40% aqueous gelatin solution for the undercoat layer at 40°C, 120 parts of water and 556 parts of methanol were added and sufficiently mixed and stirred, then 208 parts of the 5% mica dispersion were added and sufficiently mixed and stirred, and 9.8 parts of a 1.66% polyethylene oxide surfactant were added. Then, at a liquid temperature maintained at 35 to 40°C, 7.3 parts of an epoxy compound gelatin hardening agent were added to prepare a coating

solution (5.7%) for the undercoat layer to obtain a coating solution for the undercoat layer.

[0151]

<Preparation of support with undercoat layer>

Wood pulp, composed of 50 parts of LBPS and 50 parts of LBPK, was beaten with a disk refiner to a Canadian freeness of 300 ml, then had added thereto 0.5 parts of epoxylated behenate amide; 1.0 part of anionic polyacrylamide; 1.0 part of aluminum sulfate; 0.1 part of polyamidepolyamine epichlorohydrin; and 0.5 parts of cationic polyacrylamide, each in absolute dry mass ratios to the pulp, and was subjected to paper making with a long-screen paper mill to form a base paper with a basis weight of 114 g/m² and the thickness was adjusted to 100 µm by a calendaring process.

[0152]

After a corona discharge treatment on both surfaces of the base paper, polyethylene was coated with a melt extruder so as to obtain a resin thickness of 36 µm thereby forming a resin layer of a matted surface (referred to as a "rear surface"). Then, on the surface opposite to the surface bearing the above-mentioned resin layer, polyethylene containing titanium dioxide of anatase

type in 10% and a small amount of Prussian blue were coated with a melt extruder so as to obtain a resin thickness of 50 μm thereby forming a resin layer with a glossy surface (referred to as a "front surface"). On the polyethylene resin coated rear surface, after a corona discharge treatment, aluminum oxide (trade name: Alumina Sol 100, manufactured by Nissan Chemical Industries, Ltd.)/silicon dioxide (trade name: Snowtex-O, manufactured by Nissan Chemical Industries, Ltd.) = 1/2 (mass ratio) as an antistatic agent were dispersed in water and coated with a dry mass amount of 0.2 g/m^2 . Then, on the polyethylene resin coated front surface, after a corona discharge treatment, the above-described coating solution for the undercoat layer was coated with a coating amount of mica of 0.26 g/m^2 to obtain a support with an undercoat layer.

[0153]

(8) Preparation of multi-color thermal recording material

On the support with the undercoat layer, seven layers were simultaneously and successively coated in the following order from the bottom, of the thermal recording layer coating solution (c); the intermediate layer coating solution; the thermal recording layer coating solution (b); the intermediate layer coating solution; the thermal

recording layer coating solution (a); the coating solution for the light transmittance control layer; and the coating solution for the protective layer and were dried under conditions of 30°C, 30%RH and then 40°C, 30%RH to obtain a multi-color thermal recording material of example 1.

In this operation, the thermal recording layer coating solution (a) was coated such that the diazo compound (A) had a solid coating amount of 0.078 g/m²; the thermal recording layer coating solution (b) was coated such that the diazo compound (D) had a solid coating amount of 0.206 g/m² in the solution; and the thermal recording layer coating solution (c) was coated such that the electron donating dye (H) had a solid coating amount of 0.355 g/m².

[0154]

Further, the intermediate layer coating solution was coated, between (a) and (b), so as to have a solid coating amount of 2.50 g/m². The intermediate layer coating solution was coated, between (b) and (c), so as to have a solid coating amount of 3.45 g/m². Further, the coating solution for the light transmittance control layer was coated so as to have a solid coating amount of 2.35 g/m², and the coating solution for the protective layer was coated so as to have a solid coating amount of 1.60 g/m².

[0155]

[Example 2]

The multi-color thermal recording material of example 2 was prepared the same as in example 1, except that, in the preparation of the pigment dispersion for the protective layer, 29.0 parts of colloidal silica (trade name: Snowtex-O, manufactured by Nissan Chemical Industries, Ltd.) were added to 76.8 parts of the barium sulfate dispersion.

[0156]

[Comparative Example 1]

The multi-color thermal recording material of comparative example 1 was prepared the same as in example 1, except that, in the preparation of the pigment dispersion for the protective layer, the colloidal silica (trade name: Snowtex-O, manufactured by Nissan Chemical Industries, Ltd.) was not added.

[0157]

[Comparative Example 2]

The multi-color thermal recording material of comparative example 2 was prepared the same as in example 1, except that, in the preparation of the coating solution

for the protective layer, zirconium carbonate (trade name: Zircosol AC7, manufactured by Newtex Co.) was not added.

[0158]

[Comparative Example 3]

The multi-color thermal recording material of comparative example 3 was prepared the same as in example 1, except that, in the preparation of the coating solution for the intermediate layer, boric acid (4.0% aqueous solution) was not added.

[0159]

[Comparative Example 4]

The multi-color thermal recording material of comparative example 4 was prepared the same as in example 1, except that, in the preparation of the coating solution for the intermediate layer, boric acid (4.0% aqueous solution) was not added, and that, in the preparation of the coating solution for the protective layer, zirconium carbonate (trade name: Zircosol AC7, manufactured by Newtex Co.) was not added.

[0160]

(9) Evaluation Test

The multi-color thermal recording materials of the

aforementioned examples and comparative examples were subjected to the following evaluation tests. The obtained results are shown in Table 4.

[0161]

<Measurement of glossiness>

A black solid image was printed on each thermal recording material with a digital printer (trade name: NC370D, manufactured by Fuji Photo Film Co., Ltd.). On a print surface of the black solid image of each thermal recording material, the mirror surface glossiness was measured with a digital variable angle glossiness meter (trade name: UGV-5D, manufactured by SUGA TEST INSTRUMENTS CO., LTD.) with an incident angle of 20°.

[0162]

<Measurement of printing torque>

An A5-sized thermal head (model: KTJ-13 SAN24-FFA, manufactured by Kyocera Corporation.) was mounted on a jig printer equipped with a platen of a diameter of 12φ, a hardness of 40° and a pressure of 6 kg/cm (trade name: GX-3, manufactured by Matires Co.), and gradation printing was executed with conditions of a line cycle of 5.29 ms, an electric power of 0.32 W, a maximum print energy of 105.6 mJ/mm² and a transport speed of 16 mm/s. In this

operation, the torque generated between the thermal recording material and the platen roll was measured at print energies of 17, 40 and 95 mJ/mm² and was converted into a coefficient of dynamic friction.

[0163]

<Evaluation of unevenness due to load change>

A test pattern including a high energy image area (black solid band) and a low energy area (white background area) in succession was printed on each thermal recording material with a digital printer (trade name: NC370D, manufactured by Fuji Photo Film Co., Ltd.), and the level of unevenness in the density was evaluated by visual observation according to the following criteria:

-Criteria-

AA: unevenness in density not observed;

BB: slight unevenness in density observed in certain portions;

CC: high unevenness in density observed.

[0164]

<Dirt of thermal head>

With a digital printer (trade name: NC-300, manufactured by Fuji Photo Film Co., Ltd.), an A5-sized solid black image was printed continuously for 10000

sheets by randomly applying print energy (9 to 105 mJ/mm²). Regarding Dirt of the thermal head after printing, changes in the shape of a surface of the resistor element of the thermal head before and after the printing were measured with a needle-contact surface shape measuring apparatus (trade name: P-11, manufactured by KAL Tencor Corp.). The amount of dirt was calculated from the measured changes and normalized. A smaller value signifies less dirt of the thermal head.

[0165]

<Evaluation of image quality>

With a PX printer (trade name: NC-600D, manufactured by Fuji Photo Film Co., Ltd.), an A6-sized test image including areas of different print energies of 9 to 105 mJ/mm² was continuously printed for 30000 sheets. Image quality after printing was observed visually and evaluated according to the following criteria:

-Criteria-

○ : uneven density, step differences, scratches, etc.
not observed;

density uneven: slight density unevenness observed
in certain portions;

print failure: extreme density unevenness, step
differences, scratches, etc. observed.

[0166]

Table 4

	Addition amount of zirconium [*]	Addition amount of boric acid [*])	Barium sulfate/ silica ratio	Silica particle size	Printing torque			Unevenness due to load change	Glossiness	Dirt of head	Image quality ^{**}) (30000 prints)
					17 mJ/mm ₂	40 mJ/mm ₂	95 mJ/mm ₂				
Example 1	3.0 %	15 %	90/10	20 nm	0.26	0.16	0.16	AA	48	0.3	○
Example 2	3.0 %	15 %	84/16	20 nm	0.27	0.16	0.17	AA	50	0.4	○
Comp.Ex.1	3.0 %	15 %	100/0	20 nm	0.27	0.16	0.16	AA	48	12.0	print failure
Comp.Ex.2	-	15 %	84/16	20 nm	0.31	0.19	0.20	BB	42	2.0	density unevenness
Comp.Ex.3	3.0 %	-	84/16	20 nm	0.32	0.19	0.20	BB	44	3.0	density unevenness
Comp.Ex.4	-	-	84/16	20 nm	0.42	0.27	0.26	CC	24	45.0	print failure

^{*}) Represented in % by mass with respect to PVA resin

^{**}) Image quality evaluation after 30,000 prints

[0167]

According to the results in Table 4, multi-color thermal recording materials of the invention, which have a protective layer including polyvinyl alcohol and two or more kinds of ultrafine inorganic particles with different average particle sizes, and further includes boric acid and a water-soluble zirconium compound (examples 1 to 3) had excellent glossiness and suppressed unevenness due to load change (unevenness in density). Further, the multi-color thermal recording materials of the invention (examples 1 to 3) showed reduced printing torque and reduced dirt of the thermal head, thereby being capable of printing high-quality image.

In contrast, the thermal recording material of the comparative example including ultrafine inorganic particles of one average particle size only in the protective layer (comparative example 1) was inferior in that dirt accumulated on the recording head and image quality was poor. The thermal recording materials of the comparative example not including boric acid and/or water-soluble zirconium compound (comparative examples 2 to 4) were insufficient in glossiness, exhibited unevenness due to load change and the printing torque was high, thereby being inferior in quality.

[0168]

[Effects of the Invention]

The present invention can provide a thermal recording material which, when printing multiple times on the same surface at high speed and with high energy, provides high glossiness and is capable of reducing printing torque and unevenness in density, and dirt of the thermal head, thereby improving the durability thereof and recording of high-quality images.

[DOCUMENT NAME] ABSTRACT OF THE DISCLOSURE

[SUMMARY]

[OBJECT]

To provide a thermal recording material which, when printing multiple times on the same surface at high speed and with high energy, provides high glossiness and is capable of reducing printing torque and unevenness in density, improving dirtying of the thermal head and, thereby enabling the recording of high-quality images.

[MEANS FOR SOLUTION]

A thermal recording material comprising, on a support, a thermal recording layer and a protective layer which comprises at least polyvinyl alcohol and two or more kinds of ultrafine inorganic particles having different average particle sizes, wherein the thermal recording material further comprises boric acid and a water-soluble zirconium compound.

[SELECTED FIGURE]

NONE